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A COMPREHENSIVE TREATISE
ON
INORGANIC AND THEORETICAL CHEMISTRY

BY
J. W. MELLOR, D.Sc., F.R.S.

VOLUME XI

WITH 221 DIAGRAMS

LONGMANS, GREEN AND CO.
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Dedicated

TO THE

PRIVATES IN THE GREAT ARMY
OF WORKERS IN CHEMISTRY

THEIR NAMES HAVE BEEN FORGOTTEN
THEIR WORK REMAINS

PREFACE

I am very greatly obliged to my friends and colleagues Messrs. F. H. Clews, M.Sc., A.I.C., A. T. Green, F.Inst.P., A.I.C., A. Scott, M.A., D.Sc., and L. S. Theobald, B.Sc., A.R.C.Sc., for kindly reading the proofs of previous volumes, and the present volume.

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ABBREVIATIONS

aq. = aqueous
atm. = atmospheric or atmosphere(s)
at. vol. = atomic volume(s)
at. wt. = atomic weight(s)
T° or $^\circ K$ = absolute degrees of temperature
b.p. = boiling point(s)
θ° = centigrade degrees of temperature
coeff. = coefficient
conc. = concentrated or concentration
dil. = dilute
eq. = equivalent(s)
f.p. = freezing point(s)
m.p. = melting point(s)
$\text{mol(s)} = \begin{cases}\text{gram-molecule(s)}\\ \text{gram-molecular}\end{cases}$
$\text{mol(s).} = \begin{cases}\text{molecule(s)}\\ \text{molecular}\end{cases}$
mol. ht. = molecular heat(s)
mol. vol. = molecular volume(s)
mol. wt. = molecular weight(s)
press. = pressure(s)
sat. = saturated
soln. = solution(s)
sp. gr. = specific gravity (gravities)
sp. ht. = specific heat(s)
sp. vol. = specific volume(s)
temp. = temperature(s)
vap. = vapour

In the **cross references** the first number in clarendon type is the number of the volume; the second number refers to the chapter; and the succeeding number refers to the "§," section. Thus **5**. 38, 24 refers to § 24, chapter 38, volume 5.

The oxides, hydrides, halides, sulphides, sulphates, carbonates, nitrates, and phosphates are considered with the basic elements; the other compounds are taken in connection with the acidic element. The double or complex salts in connection with a given element include those associated with elements previously discussed. The carbides, silicides, titanides, phosphides, arsenides, etc., are considered in connection with carbon, silicon, titanium, etc. The intermetallic compounds of a given element include those associated with elements previously considered.

The use of **triangular diagrams** for representing the properties of three-component systems was suggested by G. G. Stokes (*Proc. Roy. Soc.*, **49**. 174, 1891). The method was immediately taken up in many directions and it has proved of great value. With practice it becomes as useful for representing the properties of ternary mixtures as squared paper is for binary mixtures. The principle of triangular diagrams is based on the fact that in an equilateral triangle the sum of the perpendicular distances of any point from the three sides is a constant. Given any three substances A, B, and C, the composition of any possible combination of these can be represented by a point in or on the triangle. The apices of the triangle represent the single components *A*, *B*, and *C*, the sides of the triangle represent binary mixtures of *A* and *B*, *B* and *C*, or *C* and *A*; and points within the triangle, ternary mixtures. The compositions of the mixtures can be represented in percentages, or referred to unity, 10, etc. In Fig. 1, pure *A* will be represented by a point at the apex marked *A*. If 100 be the

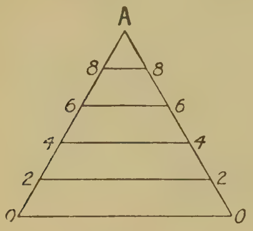

FIG. 1.

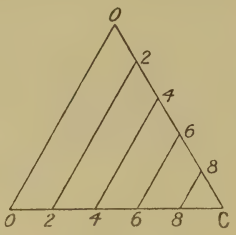

FIG. 2.

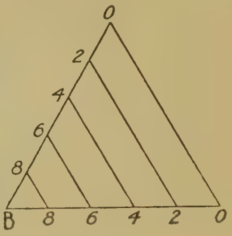

FIG. 3.

standard of reference, the point *A* represents 100 per cent. of *A* and nothing else; mixtures containing 80 per cent. of *A* are represented by a point on the line 88, 60 per cent. of *A* by a point on the line 66, etc. Similarly with *B* and *C*—Figs. 3 and 2 respectively. Combine Figs. 1, 2, and 3 into one diagram by superposition, and Fig. 4 results. Any point in this

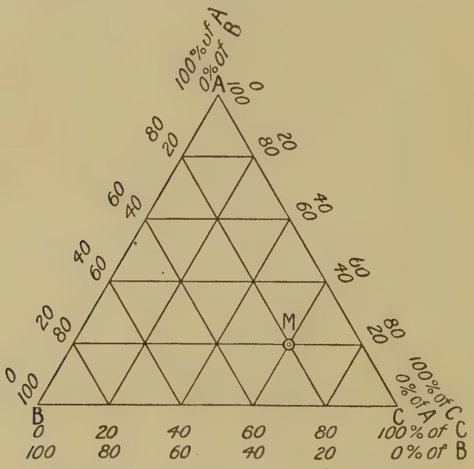

FIG. 4.—Standard Reference. Triangle.

diagram, Fig. 4, thus represents a ternary mixture. For instance, the point *M* represents a mixture containing 20 per cent. of *A*, 20 per cent. of *B*, and 60 per cent. of *C*.

CHAPTER LIX

TELLURIUM

§ 1. The History and Occurrence of Tellurium

Up to near the end of the eighteenth century, the peculiar mineral known as *white gold-ore* or *grey gold-ore*, occurring in the sandstone near Zalathna, Transylvania, appears to have been considered by chemists and mineralogists as a kind of alloy of antimony and bismuth. One variety of the mineral was called *Gelberz, Schrifterz, Blättererz,* or *blätterige Graugolderz* by G. A. Scopoli;[1] and *or gris lamelleux* by I. Eques a Born. Later, it became the *Nagyager Erz* of A. G. Werner; the *Blattertellur* of J. F. L. Hausmann; and the *nagyagite* of W. Haidinger. Another variety, *Weissgolderz,* was called *or blanc d'Offenbanya,* or *or graphique,* or *aurum graphicum,* by I. Eques a Born; *prismatische Weissgolderz* by J. E. von Fichtel; and *aurum bismuticum* by J. G. Schmeisser. The *Weissgolderz* was afterwards called *sylvane graphique* by A. J. M. Brochant; *Schriftellur* by J. F. L. Hausmann; *Schrifterz* by J. Esmark; *sylvane* by F. S. Beudant; *sylvanite* by L. A. Necker; and *aurotellurite* by J. D. Dana.

C. A. Gerrard's analysis gave: 76 per cent. of sulphur and bismuth, 18 per cent. of gold, and 6 per cent. of silver; while A. von Ruprecht's analysis gave: gold, 11·6; silver, 2·33; lead oxide, 25; iron oxide, 16·66; arsenic oxide, 1·00; antimony oxide, 2·08; sulphur, 41·66 per cent.

In 1782, F. J. Müller von Reichenstein[2] showed that the *Weissgolderz* gave no indication of the presence of either antimony or bismuth, and he suspected that it contained a new metal, which he called *metallum problematicum* or *aurum paradoxum.* T. Bergman received a sample of the mineral, and examined it by the blow-pipe. He said that the metal is of a different nature from antimony, but he did not venture to give a decided opinion; although, according to P. Diergart, T. Bergman concluded that F. J. Müller von Reichenstein had discovered a new element. About 1789, P. Kitaibel also suspected the presence of a new element; and, a few years later, M. H. Klaproth extracted the unknown metal and observed a number of its properties, from which he concluded that the mineral contains a peculiar, distinct metal essentially different from every other metallic substance hitherto known; and he added that since these properties had previously been described in the crude mineral, it is to F. J. Müller von Reichenstein that the merit belongs of having first suspected in Weissgolderz a new and distinct metal, and of having demonstrated its probable existence. This was verified by J. F. Gmelin. M. Tihavsky tried to show that tellurium and antimony are the same; but the attempt was abortive.

Tellurium occurs in only a few places and in small quantities; it is less abundantly distributed than any other element of the sulphur family. It rarely occurs in the elemental state, and it is present only in tellurides and in a few oxidized ores. According to F. W. Clarke and H. S. Washington,[3] the igneous rocks on the earth's crust contain 8×10^{-2} per cent. of sulphur, $n\times10^{-8}$ per cent. of selenium, and $n\times10^{-9}$ per cent. of tellurium; and tellurium is about as abundant as gold. J. H. L. Vogt gave for sulphur 6×10^{-2}, selenium $n\times10^{-9}$, and tellurium $n\times10^{-10}$ per cent. W. Vernadsky gave $0{\cdot}0_56$ for the percentage amount, and $0{\cdot}0_65$ for the atomic proportion. H. A. Rowland[4] failed to detect the lines of tellurium in the solar spectrum ; and the subject was discussed by F. E. Baxendall. According to C. E. St. John, it is yet uncertain whether or not tellurium lines occur in the solar spectrum.

The occurrence of native tellurium at Nagyag, Transylvania, was discussed by V. R. von Zepharovich ;[5] at Oravicza, Transylvania, by B. von Cotta ; in Ruda, Erzgebirge, by F. Berwerth; in the vicinity of Zalathna, by M. H. Klaproth, W. Petz, J. Loczka, V. R. von Zepharovich, L. Tokody, G. Rose, A. Brezina, H. von Foullon, and G. Benkö ; in Asia Minor, by G. Cesaro ; in Colorado, by W. P. Headden, G. Rolland, B. Silliman, F. A. Genth, G. vom Rath ; in California, by D. L. Mathewson, G. Kustel, and F. A. Genth ; in Chile, by E. Bertrand ; in New South Wales, by A. Liversidge; in Western Australia, by R. W. E. MacIvor, M. Maryansky, and A. Frenzel ; and in the Transvaal, by A. Frenzel. The following are analyses of some native tellurium selected from these reports :

	Te	Se	S	Au	Ag	Fe	Gangue
Zalathna . . .	80·39	0·33	9·26	0·33	—	8·55	1·54
Zalathna . . .	97·92	trace	—	0·15	—	0·53	1·62 (Cu)
Magnolia (Colorado) .	96·91	—	—	0·60	0·07	—	2·42
Ballerat (Colorado) .	93·64	—	—	2·18	1·15	0·18	2·85
John Jay (Colorado) .	97·94	—	—	1·04	0·20	0·89	0·32 (Zn)
Gunnison (Colorado) .	99·45	0·40	—	—	—	0·11	—
West Australia . .	96·935	—	—	2·399	—	—	—

Tellurium occurs combined with gold, silver, bismuth, and many other metals. It is rather a nuisance in certain auriferous districts where the gold and silver ores are unfit for amalgamation, etc., because the telluride ores do not give up their gold to mercury, to cyanide, or to chlorine ; the ores also concentrate badly ; they are difficult to roast on account of their low m.p. and gold is lost during the removal of the tellurium. The telluride ores are smelted either with lead or copper ores which act as a flux. Large amounts of tellurium enter the copper matte. The mattes are then bessemerized, and the copper refined by electrolysis. The copper contains not far from 0·04 per cent. of tellurium. The slimes contain most of the tellurium, antimony, cæsium, and bismuth together with silver and gold. The chief tellurium minerals are the tellurides ; and the oxidized minerals are represented by tellurous acid, the tellurites and the tellurates. The **tellurides** include *tellurium bismuth glance*, Bi_2Te_3 ; *tetradymite*, Bi_2Te_2S ; *wehrlite*, Bi_7Te_7Ag ; and *pilasonite*, Bi_3Te_2—as well as the non-homogeneous *oruetite*, $Bi_2Te_3.Bi_2S_3$. There are also *joseite*, Bi_3TeS ; *grünlingite*, Bi_4S_3Te ; *rickardite*, Cu_4Te_3 ; *altaite*, PbTe ; *melonite*, Ni_2Te_3 ; *coloradoite*, HgTe ; *stützite*, Ag_4Te(monoclinic) ; *hessite*, Ag_2Te(cubic) ; *empressite*, AgTe ; *petzite*, $(Ag,Au)_2Te$; *muthmannite*, (Ag,Au)Te ; *sylvanite*, $AuAgTe_4$; *krennerite*, $(Au,Ag)Te_2$; *goldschmidtite*, Au_2AgTe_6 ; *calaverite*, $AuTe_2$; *antamokite*, a gold silver telluride ; *nagyagite*, $Au_2Sb_2Pb_{10}Te_6S_{15}$; *talapite*, $Bi(S,Te)_3AG_3$; *vondiestite*, $(Ag,Au)_5BiTe_4$; *goldfieldite*, $5CuS.(Sb,Bi,As)_2(S,Te)$; *arsenotellurite*, $Te_2As_2S_7$; *coolgardite*, a mixture of coloradoite, petzite, calaverite, and sylvanite ; *kalgoorlite*, a mixture of coloradoite, petzite, and tellurium ; *white tellurium*, an antimonial telluride of gold, silver, and lead ; and likewise also *Gelberz*, and *müllerite ;* and *henryite*, a mixture of lead telluride and pyrites. The oxidized minerals include the **tellurites**—*tellurite*, TeO_2 ; *durdenite*, $Fe_2(TeO_3)_3.4H_2O$, with a little selenium ; and *emmonsite*, a mixture of ferric tellurite, etc.—and the **tellurates**—*montanite*, $Bi(OH)_2TeO_4$; *magnolite*, Hg_2TeO_4 ; and *ferrotellurite*, $FeTeO_4$.

According to A. Cossa,[6] tellurium occurs among the eruption products of Vulcana, Lipari Islands. F. Zambonini and L. Coniglio observed it amongst the products of Vesuvius. E. Divers and T. Shimidzu found 0·17 per cent. of tellurium in the orange-red sulphur of Japan, and tellurium was also found in the chamber-mud of the sulphuric acid works at Osaka, Japan. D. Playfair observed about 0·002 per cent. of tellurium in the flue-dust of a furnace roasting Spanish pyrites. D. Forbes[7] reported 5·9 per cent. of tellurium in the native bismuth of Bolivia ; F. A. Genth, 0·042 per cent. ; and R. Schneider, 0·14 per cent. The presence of tellurium in commercial bismuth preparations—*e.g.* the oxynitrate—was discussed by

J. O. Braithwaite, E. Isnard, G. Brownen, M. Reisert, E. A. Letts, Bonz und Söhne, etc. The gold and silver ores of Colorado and other American States were discussed by C. Whitehead,[8] C. Vincent, H. J. Burkart, F. A. Genth, C. Palache, W. P. Headden, etc. E. Thomson found tellurium in Canada, in the ores of Montbray, Quebec. C. Rössler, and K. B. Heberlein found it in the silver ores of Spezia, Italy, when it occurs associated with platinum telluride; P. Krusch, and L. J. Spencer, in the gold ores of Kalgoorlie, West Australia; E. Weckwarth, near Quisque, in Peru; and it has also been reported in the gold ores of Offenbanya, Siebenbürgen. K. B. Heberlein found tellurium in the lead ores of Tasmania, and of Spezia, Italy; and C. H. Fulton, T. Egleston, E. Keller, and V. Lenher, in American copper ores. A. Schoep found up to 0·67 per cent. tellurium trioxide in fourmarierite. E. Priwoznik,[9] and S. Skowronsky made some general observations on the occurrence of tellurium.

REFERENCES.

[1] F. J. Müller von Reichenstein, *Phys. Arb. Freunde Wien*, **3**. 48, 1785; A. von Ruprecht, *ib.*, **1**. 86, 1783; G. A. Scopoli, *Ann. Hist. Nat.*, **3**. 107, 1777; I. Eques a Born, *Lythophylacium Bornianum*, Prague, **1**. 68, 1772; *Catalogue méthodique et raisonné de la collection des fossiles de Mlle. Eleonore de Raab*, Vienna, **2**. 467, 1790; F. S. Beudant, *Traité élémentaire de minéralogie*, Paris, **2**. 539, 1832; A. J. M. Brochant, *Traité de minéralogie*, Paris, 1800; J. F. L. Hausmann, *Handbuch der Mineralogie*, Göttingen, 130, 1813; W. Haidinger, *Handbuch der bestimmenden Mineralogie*, Wien, 566, 1845; A. G. Werner, *Letztes Mineralsystem*, Freiberg, 24, 1817; *Berg. Journ.*, **2**. 373, 1789; J. Esmark, *ib.*, **2**. 10, 1798; L. A. Necker, *Le régne minéral ramené aux méthodes de l'histoire naturelle*, Paris, 1835; J. D. Dana, *A System of Mineralogy*, New York, 390, 1837; J. E. von Fichtel, *Mineralogische Bemerkungen von den Karpathen*, Wien, **2**. 108, 1791; *Mineralogische Aufsatze*, Wien, 124, 1794; C. A. Gerrard, *Grundriss des Mineralsystems*, Berlin, 210, 1786; J. G. Schmeisser, *A System of Mineralogy*, London, **2**. 28, 1795.

[2] F. J. Müller von Reichenstein, *Phys. Arb. Freunde Wien*, **1**. 1, 1782; **3**. 48, 1785; T. Bergman, *De tubo ferruminatorio*, Vindelbonæ, 1779; P. Kitaibel, *Gehlen's Journ.*, **1**. 460, 1803; M. Tihavsky, *Gilbert's Ann.*, **11**. 246, 1802; *Nicholson's Journ.*, **2**. 62, 1801; M. H. Klaproth, *Mem. Akad. Berlin*, **50**. 17, 1798; *Beiträge zur Chemischen Kenntniss der Mineralkörpen*, Berlin, **3**. 1, 1802; London, **2**. 1, 1804; *Crell's Ann.*, **1**. 91, 1798; *Gilbert's Ann.*, **12**. 246, 1802; P. Diergart, *Zeit. angew. Chem.*, **33**. 299, 1920; B. Kirwan, *Elements of Mineralogy*, London, **2**. 324, 1798; A. G. Werner, *Letztes Mineralsystem*, Freiberg, 1817; T. Berdell, *Zeit. Kryst.*, **2**. 1, 1877; *Proc. Amer. Phil. Soc.*, **17**. 133, 1877; J. F. Gmelin, *Comment. Gött.*, **14**. 20, 1799.

[3] F. W. Clarke and H. S. Washington, *Proc. Nat. Acad.*, **8**. 108, 1922; *The Composition of the Earth's Crust*, Washington, 1924; J. H. L. Vogt, *Zeit. prakt. Geol.*, **6**. 226, 314, 413, 1898; **7**. 10, 274, 1899; W. Vernadsky, *Essai de minéralogie descriptive*, St. Petersburg, **1**. 121, 740, 1914; *Geochimie*, Paris, 16, 1924; A. E. Fersman, *Bull. Acad. St. Petersburg*, (6), **6**. 367, 1912.

[4] H. A. Rowland, *Johns Hopkins Univ. Circular*, 85, 1891; *Amer. Journ. Science*, (3), **41**. 243, 1891; *Chem. News*, **63**. 133, 1891; F. E. Baxendall, *Researches on the Chemical Origin of various Lines in Solar and Stellar Spectra*, London, 1910; C. E. St. John, *Astrophys. Journ.*, **70**. 160, 1930.

[5] V. R. von Zepharovich, *Mineralogisches Lexikon für das Kaiserthum Osterreich*, Wien, **1**. 443, 1859; **3**. 246, 1893; M. H. Klaproth, *Beiträge zur chemischen Kenntniss der Mineralkörper*, Berlin, **3**. 1, 1802; G. Rose, *Abhand. Akad. Berlin*, 84, 1849; *Pogg. Ann.*, **77**. 147, 1849; W. Petz, *ib.*, **57**. 477, 1842; A. Brezina, *Ann. naturhist. Hofmuseum*, **1**. 137, 1886; H. von Foullon, *Verh. geol. Reichsanst. Wien*, 269, 1884; L. Tokody, *Centr. Min.*, 114, 1929; G. Benkö, *Orvis Termt. Ertesite*, **12**. 217, 1887; *Zeit. Kryst.*, **14**. 387, 1888; J. Loczka, *ib.*, **20**. 319, 1892; A. Frenzel in C. Hintze, *Handbuch der Mineralogie*, Leipzig, **1**. i, 104, 1904; B. Silliman, *Amer. Journ. Science*, (3), **8**. 27, 1874; F. A. Genth, *ib.*, (2), **45**. 313, 1868; (3), **8**. 27, 1874; *Proc. Amer. Phil. Soc.*, **14**. 2, 1874; **17**. 113, 1877; G. vom Rath, *Verh. naturhist. Ver. Bonn*, 296, 1884; P. H. van Diest, *Proc. Colorado Scient. Soc.*, **2**. 50, 1886; W. P. Headden, *ib.*, **7**. 141, 1903; B. von Cotta, *Erzlagerstätten in Banat und Serbien*, Wien, 59, 1865; G. Kustel, *Min. Scient. Press.*, **10**. 306, 1865; *Bull. Soc. Chim.*, (2), **20**. 174, 1873; *Osterr. Zeit. Berg. Hütt.*, **21**. 109, 1873; *Berg. Hütt. Ztg.*, **25**. 128, 1866; D. L. Mathewson, *ib.*, **24**. 274, 1865; E. Bertrand, *Neues Jahrb. Min.*, 465, 1870; A. Liversidge, *Journ. Roy. Soc. New South Wales*, **16**. 39, 1883; M. Maryansky, *Zeit. prakt. Geol.*, **5**. 72, 1897; G. Rolland, *Ann. Mines*, (7), **13**. 159, 1878; R. W. E. MacIvor, *Chem. News*, **82**. 272, 1900; G. Cesaro, *Bull. Acad. Belg.*, 255, 1908; F. Berwerth, *Mitt. Min. Ges. Wien*, 19, 1916; T. A. Richard, *Eng. Min. Journ.*, **114**. 708, 752, 972, 1922; S. Koch, *Ban. Koh. Lapok*, **62**. 425, 449, 1929.

[6] A. Cossa, *Zeit. anorg. Chem.*, **17**. 205, 1898; E. Divers and T. Shimidzu, *Chem. News*, **44**. 229, 1881; **48**. 286, 1883; **49**. 26, 1884; D. Playfair, *ib.*, **39**. 345, 1879; F. Zambonini and L. Coniglio, *Ann. Osserv. Vesuviano*, (3), **2**. 3, 1925.

[7] D. Forbes, *Phil. Mag.*, (4), **29**. 1, 1865; R. Schneider, *Journ. prakt. Chem.*, (2), **23**. 78, 1881;

F. A. Genth, *Amer. Journ. Science*, (2), **28**. 247, 1859; M. Reisert, *Deut. Med. Ztg.*, 19, 1885; G. Brownen, *Pharm. Journ.*, (3), **6**. 561, 1876; E. A. Letts, *ib.*, (3), **9**. 405, 1879; J. O. Braithwaite, *Chemist Druggist*, **26**. 122, 1884; *Amer. Druggist*, **13**. 88, 1884; Bonz und Söhne, *Schweiz. Wochschr. Pharm.*, **43**. 197, 1905; E. Isnard, *Journ. Pharm. Chim.*, (7), **27**. 216, 1923.

[8] C. Whitehead, *Journ. Amer. Chem. Soc.*, **17**. 889, 1895; E. Keller, *ib.*, **19**. 771, 1897; **22**. 241, 1900; V. Lenher, *ib.*, **21**. 347, 1899; **24**. 355, 1902; C. H. Fulton, *ib.*, **20**. 586, 1898; C. Vincent, *Bull. Soc. Chim.*, (3), **27**. 23, 1902; A. Schoep, *Bull. Soc. Chim. Belg.*, **33**. 558, 1924; H. J. Burkart, *Neues Jahrb. Min.*, 476, 1873; Anon., *Berg. Hütt. Ztg.*, **53**. 321, 1894; P. Krusch, *Zeit. prakt. Geol.*, **11**. 321, 369, 1903; E. Thomson, *Geol. Stud. Univ. Toronto*, 27, 1928; W. P. Headden, *Proc. Colorado Scient. Soc.*, **7**. 141, 1905; C. Palache, *Amer. Journ. Science*, (4), **10**. 419, 1900; L. J. Spencer, *Min. Mag.*, **13**. 268, 1903; C. Rössler, *Zeit. anorg. Chem.*, **15**. 405, 1897; K. B. Heberlein, *Berg. Hütt. Ztg.*, **54**. 41, 1895; *Beiträge zur Kenntniss des Tellurs*, Basel, 1898; T. Egleston, *Chem. News*, **47**. 51, 1883; F. A. Genth, *Amer. Journ. Science*, (2), **28**. 247, 1859; E. Weckwarth, *Mining Journ.*, **85**. 523, 1909.

[9] E. Priwoznik, *Vorkommen von Tellur und Gewinnung aus seinen Erzen*, Wien, 1893; *Oesterr. Zeit. Berg. Hütt.*, **45**. 219, 1897; S. Skowronsky, *Min. Ind.*, **31**. 621, 1922; E. Thomson, *Canadian Min. Journ.*, **46**. 1187, 1924; I. A. Richard, *Eng. Min. Journ.*, **114**. 972, 1922.

§ 2. The Extraction of Tellurium

According to M. H. Klaproth,[1] native tellurium—containing, say, 97 per cent. of tellurium associated with iron, gold, and sulphur—can be dissolved in aqua regia; the soln. diluted with as much water as can be added without producing a precipitate, and treated with an excess of potash-lye. The filtrate is neutralized with hydrochloric acid. The precipitated tellurium dioxide is washed, dried, mixed with oil or with one-tenth its weight of charcoal, and heated in a glass retort. The reduced tellurium is found partly at the bottom of the retort, and partly as a sublimate.

J. J. Berzelius extracted tellurium from *tetradymite*—containing approximately 60 per cent. of bismuth, 36 of tellurium, and 4 of sulphur—by making the finely powdered ore into a stiff paste with sodium and potassium carbonates and olive oil; and heating the product, in a closed porcelain crucible, gradually to carbonize the oil, and afterwards to a white-heat. The object here is to separate the sulphur, selenium, and arsenic. The arsenic volatilizes and the sulphur and selenium remain in soln. after the tellurium has been precipitated by a current of air. The mass is cooled out of contact with air, quickly pulverized, quickly washed with air-free water, and a current of air passed through the filtrate to precipitate the tellurium. The filtrate containing tellurium sulphide (and selenide) and alkali sulphide is treated with hydrochloric acid to precipitate the tellurium. The washed tellurium is then fused, and distilled in a current of hydrogen so as to separate it from the gold, iron, manganese, and copper. F. Becker used a similar process. A. Schuller said that the distillation is easily conducted in vacuo. F. Wöhler found that the vacuum distillation in hydrogen removes the selenium as hydrogen selenide; and E. Priwoznik, that the selenium is similarly removed from molten tellurium in a current of hydrogen. J. J. Berzelius said that a trace of selenium always remains associated with the tellurium distilled in hydrogen. F. Stolba treated powdered tetradymite with hydrochloric acid to remove the limestone; and heated the washed residue with conc. hydrochloric acid, with the gradual addition of nitric acid, until the residue is white. As much water was added to the cold liquid as could be done without the separation of tellurium; iron was then added to the filtered soln., when crude tellurium, containing bismuth and copper, was precipitated. In another process, the powdered mineral was heated with sulphuric acid of sp. gr. 1·842 so long as sulphur dioxide was given off. The liquid was diluted with water, and the tellurium precipitated from the filtrate by means of iron; the residual matter was treated with conc. hydrochloric acid, and tellurium precipitated from the soln. by iron, or by sodium hydrosulphite. The tellurium was purified by dissolution in nitric acid, the liquid made alkaline with soda-lye, and the tellurium precipitated by glucose. The extraction of tellurium from bismuth ores was discussed by E. Matthey. E. Priwoznik, F. M. Horn, and J. Löwe employed modifications of the process for other minerals and ores. F. M. Horn dissolved the ore from the Allerheiligen Mine, Siebenburg, in boiling conc. sulphuric acid, and precipitated the silver with hydrochloric acid, and the tellurium by zinc.

J. J. Berzelius obtained tellurium from *silver telluride*—containing approximately 35 per cent. of tellurium, 46 to 61 of silver, and 1 to 18 of gold—by heating the powdered mineral in a current of chlorine, when silver chloride, and volatile tellurium tetrachloride are formed. There escapes a mixture of sulphur, selenium, and antimony chlorides. The tellurium tetrachloride is dissolved in dil. hydrochloric acid, and the tellurium precipitated by sodium hydrosulphite. The tellurium is purified by distillation in hydrogen. J. J. Berzelius also obtained tellurium by fusing the powdered ore with a mixture of potassium nitrate and carbonate in a silver crucible not quite to redness. When the black mass becomes reddish-grey, the temp. is increased to redness, and the mass allowed to cool. It is then lixiviated with water, and filtered. The clear liquid, which becomes turbid when heated, is evaporated to a small vol., mixed with a large proportion of powdered charcoal, and evaporated to dryness. The product is heated in a covered crucible, and then treated as in the extraction of tellurium from tetradymite. H. Hess employed a somewhat similar process. J. J. Berzelius also heated the native silver telluride with conc. nitric acid—free from chlorine. When all is oxidized, the liquid is evaporated to dryness; the dry mass extracted with water; and the residual tellurium dioxide mixed with sodium carbonate and oil as in the extraction of tellurium from tetradymite.

P. Berthier obtained tellurium from finely powdered *nagyagite*—containing approximately 30 per cent. of tellurium, and 50 per cent. of lead along with some gold, copper, antimony, and sulphur—by repeatedly boiling with conc. hydrochloric acid, and washing with boiling water; the residue was treated with nitric acid, and the decanted liquid evaporated to dryness; the resulting tellurium dioxide was dissolved in hydrochloric acid, and the tellurium precipitated with sulphurous acid. P. Berthier also fused the powdered mineral with a mixture of potassium nitrate and carbonate, and precipitated the tellurium from the acidified extract by means of iron. F. Stolba extracted the powdered mineral with hydrochloric acid, digested the residue with aqua regia, and added water so long as a precipitate—tellurium dioxide and antimony oxychloride—was formed. The gold was precipitated from the filtrate by ferrous sulphate, and the tellurium by iron in the presence of a little stannous chloride. The mixture of tellurium dioxide and antimony oxychloride was boiled with conc. soda-lye, and the tellurium precipitated from the alkaline liquor by glucose. According to B. Brauner, the precipitate obtained by diluting the above-indicated soln. with water may also contain basic tellurites which are not completely decomposed by the boiling soda-lye; if basic copper tellurite is formed, some copper may pass into soln., and be precipitated as cuprous oxide by the glucose. E. Donath, and L. Kastner used modifications of the process. J. Farbaky recommended the following process for extracting tellurium on a large scale from gold-tellurium ores:

The ore is slowly thrown into boiling conc. sulphuric acid, when lead, copper, zinc, tellurium, and also a portion of the silver compounds present go into soln., gold and silicic acid remaining undissolved. The product is then heated with water containing from 10 to 15 per cent. of hydrochloric acid, when the latter precipitates the dissolved silver and dissolves the hydrated tellurium oxide precipitated by the water. On filtering, a residue of gold and silver is obtained which is worked up separately. Sulphur dioxide is passed through the filtrate, and as this takes place in sulphuric or hydrochloric acid soln., only tellurium and selenium are thrown down. This residue is found to contain from 72–85 per cent. of tellurium, and after a repetition of the process, the percentage is increased to 97–98. The crude powder is melted and cast in moulds.

A. von Schrötter treated impure nagyagite with hydrochloric acid to remove soluble carbonates, etc.; and afterwards digested with aqua regia—with an excess of hydrochloric acid until the insoluble residue was white. Water, and hydrochloric acid were added to keep the tellurium dioxide in soln. The liquid was filtered from the silver chloride, and the soln. treated with ferrous sulphate, oxalic acid, or glycerol in a neutralized soln., to remove gold. The filtrate was treated with sulphur dioxide whereby scarlet-red selenium was first precipitated, and afterwards dark-grey tellurium. This was melted under a layer of sodium hydroxide. E. Priwoznik, F. M. Horn, H. Schnitzler, H. Schwarz, and J. Löwe used modifications of this process. W. Pethybridge discussed the extraction of tellurium from gold ores.

M. Shimose extracted tellurium from chamber-mud in the sulphuric acid works of Osaka, Japan, by digesting it with a warm soln. of potassium cyanide and sodium carbonate; the mixture was diluted with water and boiled; the filtrate was strongly acidified with sulphuric acid, treated with a little nitric acid, and the tellurium precipitated as sulphide by a current of hydrogen sulphide. The yellow sulphuric acid from the chambers was treated in a similar manner. The precipitates were melted with potassium cyanide, and the tellurium precipitated from an aq. soln. of the melted mass by the passage of a current of air. C. Whitehead said that the slimes obtained in the electrolytic refining of copper may contain much tellurium. The slimes are digested with hydrochloric acid, and the resulting soln. is decanted from the insoluble siliceous matters, and poured into water. Tellurium dioxide, along with some antimony oxychloride, is precipitated. The precipitate is dissolved in conc. hydrochloric acid and treated with sulphur dioxide when a red precipitate, consisting largely of selenium, separates out; the filtrate is diluted and again treated with sulphur dioxide when the tellurium is precipitated. The tellurium can be further purified by fusion with potassium cyanide when potassium telluride K_2Te is formed. A current of air is passed through the aq. soln. $2K_2Te+2H_2O+O_2=4KOH+2Te$. The precipitated tellurium is then fused and distilled in a current of hydrogen. Several of the tellurium ores can be treated with acid in a similar way, or fused with potash or soda, or with a mixture of sodium carbonate and potassium nitrate. In the case of the alkali fusion, the tellurate is extracted with water, treated with hydrochloric acid, and afterwards with sulphur dioxide, when glucose or sugar precipitates tellurium from soln. of alkali tellurates. Observations on this subject were made by E. Keller, V. Lenher, A. T. von Gersdorff and W. L. Kölreuter, A. Wehrle, and F. D. Crane. The extraction of tellurium from lead and silver ores was discussed by K. B. Heberlein.

P. Hulot fused the tellurate with potassium nitrate, and, on extracting the cold mass with water, there remained insoluble potassium tellurate, $K_2Te_4O_{13}$, which furnishes tellurium when suspended in water and reduced with nascent hydrogen from zinc and hydrochloric acid, or aluminium and alkali-lye.

R. W. E. MacIvor found that when the vapour of sulphur monochloride is passed over tellurium minerals—native tellurium, calcinite, etc.—the tellurium is volatilized as the tetrachloride. The solid is washed with carbon disulphide, dissolved in hydrochloric acid, and the tellurium precipitated by potassium hydrosulphite.

According to A. Gutbier, the above described methods of purification furnish crude tellurium contaminated with foreign metals—copper, silver, gold, zinc, arsenic, antimony, bismuth, iron, etc.—as well as by sulphur, selenium, silica, etc. Owing to the anomaly in the at. wts. of iodine and tellurium—**1**. 6, 6—tellurium has been tortured in numerous ways in order to find if the presence of a small proportion of some unsuspected impurity would account for the discrepancy. The element was obdurate—the results were nugatory. The impurities in selenium were removed by converting the selenium to the dioxide and heating the product nearly to its m.p. in air, when all but a trace of the selenium is volatilized as the dioxide; the sulphur and selenium can be removed by oxidizing the elements to telluric acid, etc., adding barium chloride to precipitated barium sulphate and selenate. H. Rose removed sulphur by heating the mixture with aqua regia, evaporating with hydrochloric acid, and precipitating the tellurium by sulphur dioxide. H. Rose also melted the crude tellurium with potassium cyanide in an atm. of hydrogen—

potassium telluride, selenocyanate, and sulphocyanate are formed. The telluride is then treated as indicated below for crude tellurium. A. Oppenheim observed that when the crude tellurium is heated on a water-bath with a soln. of potassium cyanide, only a little tellurium, but all the sulphur and selenium, pass into soln. Hydrochloric acid added to the soln. precipitates the selenium. A current of air passed through the soln. converts the tellurium into alkali tellurite and the soln., when treated with sulphur dioxide, gives a precipitate of tellurium. H. Rose, and M. Shimose added that tellurium is only slightly attacked by a boiling soln. and it passes into soln. in a form not precipitable by air, or by a hot soln. of potassium hydroxide and glucose, but which, like selenium, is precipitable by hydrochloric acid. A. von Schrötter, E. Priwoznik, C. Alexi, and M. Shimose said that when a conc. hydrochloric acid soln. is treated with sulphur dioxide, the selenium is first precipitated, and this is followed by grey tellurium. The process was discussed by J. J. Berzelius, E. Priwoznik, and A. von Schrötter. This subject has been discussed by E. Keller, and his results are summarized in Figs. 1 and 2 of the preceding chapter. F. D. Crane replaced the sulphur dioxide by hydrazine, hydroxylamine, or magnesium, but P. Köthner said that these precipitants offer no advantages over sulphur dioxide. E. Divers and M. Shimose worked with sulphuric in the place of hydrochloric acid. They said that selenium and tellurium are sharply distinguished from each other in their behaviour towards sulphur dioxide in the presence of sulphuric acid, and absence of hydrochloric acid. With precautions easy to be observed, the whole of the selenium is precipitated without a trace of the tellurium accompanying it. The sulphur dioxide soln. must be added to the undiluted or very slightly dil. soln. of the oxidized elements in conc. sulphuric acid. Some dilution of the sulphuric acid is indeed necessary, as the precipitation of the selenium is incomplete without it, but this is most safely and simply effected by the sulphur dioxide soln. itself. H. Rose said that the precipitation by sulphur dioxide in the presence of sulphuric acid alone is imperfect, but, added E. Divers and M. Shimose, this is only the case when the conc. of the sulphuric acid is too low. In the sulphuric acid process, the crude tellurium is heated with conc. sulphuric acid to form a colourless soln., and until no more sulphur dioxide is evolved ; four vols. of sulphurous acid are added, and only the selenium is precipitated.. The soln. is warmed on a sand-bath, diluted and filtered. The tellurium is then precipitated from the filtrate by adding hydrochloric acid, and passing a current of sulphur through the liquid. M. Shimose said that when an alkaline tellurite soln. is boiled with glucose, the tellurium is first precipitated and afterwards the selenium. F. Stolba made some observations on this subject.

B. Brauner purified tellurium by dissolving it in hydrochloric acid mixed with as little nitric acid as possible, and removing the nitric acid by repeated evaporation with hydrochloric acid. The soln., at 60° to 70°, is treated with sulphur dioxide to precipitate the selenium and tellurium which may be contaminated with lead or copper. The dry product is fused with five times its weight of potassium cyanide in an atm. of hydrogen to protect it from air. The cold mass is extracted with water, and a current of air passed through the claret-red soln. of potassium telluride. The washed and dried precipitate of tellurium is distilled in a current of hydrogen.

According to P. Köthner, tellurium may be separated from its common impurities (copper, silver, gold, bismuth, antimony, arsenic, and selenium) by dissolving the crude substance in hydrochloric acid containing a little nitric acid, evaporating off the excess of the latter reagent, diluting the cooled soln. with water until the deep yellow colour of tellurium tetrachloride disappears, filtering from the precipitate of silver chloride and the oxychlorides of antimony and bismuth, and treating the warm filtrate with sulphur dioxide. The treatment is repeated, and by fractional precipitation two or three times, and collecting the middle fraction, pure tellurium is obtained. The first fractions contain arsenic, whilst the third fraction shows traces of copper and gold. The element may be obtained in a crystalline form by passing sulphur dioxide into a hot soln. of the tetrachloride in conc. hydrochloric acid (20·3 per cent.); the crystals being opaque with a silvery lustre.

L. Staudenmaier obtained tellurium of a high degree of purity by dissolving freely powdered crude tellurium in dil. nitric acid; evaporating the soln. with conc. nitric acid, and filtering. The tellurium is then precipitated with sulphur dioxide, and washed with hydrochloric acid and water. It is then dissolved in an excess of dil. nitric acid, and a slight excess of chromic acid is added. The soln. is evaporated for crystallization, with the crystals washed with nitric acid and dissolved in a small quantity of water. The soln. is treated with a few drops of alcohol to reduce any chromic acid remaining, and precipitated by the addition of nitric acid. Finally, the product is dissolved in water and evaporated to dryness on the water-bath—telluric acid remains. This reduces to tellurium dioxide when heated, and it can be reduced to tellurium by heating it in hydrogen, or by the action of sulphur dioxide. P. Köthner said that this product still contains spectroscopic traces of copper and silver.

D. Klein and L. Morel dissolved the tellurium in conc. nitric acid, and evaporated the soln. for crystallization. The basic nitrate crystallizes out leaving the other metal nitrates in soln. The product after washing with hot water, is heated to form tellurium dioxide. This is dissolved in hydrochloric acid, and the tellurium precipitated with sulphur dioxide. J. F. Norris, H. Fay and D. W. Edgerly dissolved the oxide obtained from the purified basic nitrate in hydrochloric acid, precipitated the tellurium with sulphur dioxide, and distilled the resulting metal. P. Köthner said that the basic nitrate is conveniently prepared by dissolving small quantities of tellurium in a slight excess of nitric acid and evaporating the soln. obtained from several experiments. In this way, the separation of tellurium is reduced to a minimum. This salt, however, even after repeated crystallization, still contains traces of silver and copper. According to P. Köthner, tellurium can be separated from all other elements except antimony by distillation in a vacuum, and since this element is removed in purifying the basic nitrate, it follows that a combination of the two processes should lead to the production of pure tellurium. The product obtained by reducing the recrystallized nitrate with sulphur dioxide is distilled under 9–12 mm. press. in a tube divided into segments by asbestos partitions. After repeated distillation through three or four of these compartments a specimen is obtained which is quite free from impurities. G. W. A. Kahlbaum and co-workers, and F. Krafft and L. Merz also purified the element by distillation in vacuo. K. B. Heberlein treated the crude tellurium with nitric acid (or aqua regia or, if lead was present, with boiling conc. sulphuric acid), and added an excess of aq. ammonia—the lead, bismuth, iron, etc., are precipitated as tellurites, and the filtrate was treated with an ammoniacal soln. of an ammonium magnesium salt. White magnesium tellurite was precipitated. The washed precipitate was dissolved in a little hydrochloric acid, and reprecipitated by aq. ammonia. The tellurium was precipitated from the hydrochloric acid soln. of this product by sulphur dioxide. R. Schelle boiled the crude tellurium with powdered sulphur and a soln. of sodium sulphide, and added sodium sulphite when a greyish-black precipitate of pure tellurium was obtained. Selenium, arsenic, tin, gold, and platinum are not precipitated by this method, but copper is removed by the initial treatment with sodium sulphide. F. Krafft and R. E. Lyons prepared diphenyl telluride, $Te(C_6H_5)_2$, by treating tellurium with diphenyl mercuride. O. Steiner purified this product by fractional distillation in vacuo. G. Pellini converted the purified diphenyl telluride into dibromide which was then purified by recrystallization from benzene; the dibromide was converted into telluric acid; this was reduced to tellurium, and the product distilled in vacuo.

C. Himly used an electrolytic process for purification. The cathode was made by dipping a platinum wire into molten tellurium; and it was surrounded by a woollen or linen bag; the anode was of platinum; the electrolyte, dil. potash-lye. The potassium telluride formed at the cathode is oxidized to tellurite by the oxygen at the anode. According to C. Whitehead, tellurium is readily deposited by an electric current either from an acid or alkaline soln. It has been found possible to separate tellurium from copper by adding an excess of sodium hydroxide and about 3 grms. of potassium cyanide for each grm. of copper present, and passing an electric current through the soln.; the tellurium is thrown down as a black, non-adherent precipitate which can readily be filtered off; the soln. can then be slightly acidified with sulphuric acid and the copper estimated in the usual way by electrolysis. According to F. C. Mathers and H. L. Turner, tellurium can be deposited from a soln. of 300 grms. of tellurium dioxide (49·6 per cent. TeO_2 and 46·1 per cent. Na_2TeO_3), 500 grms. of 48 per cent. hydrofluoric acid, and 200 grms. of sulphuric acid per litre, using 1·6 amp. per sq. dm. at a lead cathode at ordinary temp. The tellurium anode dissolved and the 0·9 per cent. of selenium remained in the slimes. The deposited tellurium is light grey and brittle. The deposits are less satisfactory if hydrochloric acid be substituted for hydrofluoric acid.

J. J. Berzelius[2] referred to the blue liquid containing finely-divided tellurium which is obtained when a very dil. soln. of potassium telluride is exposed to air; and B. Brauner, to the blue, greenish-blue, or violet liquid obtained by the action of sulphurous acid on a hydrochloric acid soln. of tellurium dioxide. A. Gutbier obtained **colloidal tellurium** by reducing a dil. soln. of tellurous or telluric acid by means of hydrazine hydrate, phenylhydrazine, hydroxylamine hydrochloride, hypophosphorous acid, sulphurous acid, sodium hydrosulphite. If the reduction occurs in the presence of gum arabic, or an extract of the seeds of *Plantago psyllium*, the hydrosol is *ausserordentlich beständig*. L. Lilienfeld used gelatin, gum arabic, and proteins as protective colloids. A. Gutbier and F. Resenscheck found that when an aq. soln. of telluric acid containing potassium cyanide is electrolyzed with a current of 0·5 amp., the soln. gradually becomes brownish-violet owing to the formation of tellurium in the hydrosol form; as the electrolysis is continued, the tellurium separates as a flocculent precipitate. When ammonium oxalate is substituted for potassium cyanide, the steel-blue hydrosol of tellurium is first of all formed. By dialysis, the new brownish-violet hydrosol form may be obtained in brilliantly-coloured soln., which are not decomposed after six months. According to C. Paal and C. Koch, the brown modification of colloidal tellurium is easily obtained by warming an alkaline aq. soln. of telluric acid, containing protalbic or lysalbic acid, with hydrazine hydrate on the water-bath; in neutral or alkaline soln., containing sodium protalbate or lysalbate, telluric acid is reduced by hydroxylamine only on boiling, as is tellurium dioxide by hydrazine hydrate; in these cases, the brown modification, at first formed, changes into the blue as the boiling proceeds. A. Gutbier and F. Resenscheck's brownish-violet tellurium hydrosol is probably a mixture of the brown and blue modifications. As in the case of colloidal selenium, the liquid hydrosols of tellurium, containing sodium protalbate or lysalbate, are very stable, and, on careful evaporation, yield the solid hydrosols, which are soluble in water and remain unchanged when heated to 100° in vacuo. On addition of acetic acid to the liquid hydrosols, the solid hydrosols containing protalbic or lysalbic acid are precipitated; these contain upwards of 80 per cent. of tellurium, and are very stable when protected from the atm. oxygen, the brown modification retaining its solubility after three years. P. P. von Weimarn and B. V. Maljisheff obtained colloidal tellurium by adding 0·1 grm. of the element to 5 c.c. of a boiling soln. of potassium hydroxide, sat. at the ordinary temp., and adding the soln. of the metal thus formed to 1000 c.c. of cold water, the mixture being stirred vigorously. The stability of the colloidal tellurium soln. depends directly on the peptization processes, and can be greatly increased. The soln. can also be made more stable by the addition of gelatin or similar substances. C. Levaditi found that a 30 per cent. aq. soln. of dextrose added to a 5 per cent. aq. soln. of sodium tellurite, and heated to boiling for half an hour, furnishes colloidal tellurium.

G. Bredig obtained a colloidal soln. of tellurium by the cathodic spluttering of the element. E. Müller and R. Lucas found that with an applied e.m.f. of four or more volts, in water, a tellurium cathode loses weight, and yields a colloidal soln. of tellurium. The very dil. soln. are reddish-violet in colour, the more conc. soln. are brown and opaque. The tellurium goes into soln. with an apparent valency of about 1·2, which indicates that the pulverization is not merely mechanical. The dissolution is independent of the presence of oxygen in soln. and is therefore not due to oxidation of tellurium hydride. No hydrogen is evolved at the tellurium cathode. The phenomena may be explained by assuming that the tellurium goes into soln. in the form of the Te'-ion, which then passes into bivalent tellurium ions either by direct assumption of a second charge from the electrode or by the reaction $2\mathrm{Te}'=\mathrm{Te}+\mathrm{Te}''$. In alkaline soln., the pulverization takes place also, but alkali polytellurides are also formed. In acidic soln., hydrogen is evolved and only a trace of pulverization can be observed, the discharge potential of hydrogen in the acidic soln. being lower than that required for the dissolution of tellurium. A. Gutbier and B. Ottenstein prepared a sol of tellurium by reducing telluric acid with dextrose in the presence of ammonia. The presence of tellurous acid, and absorbed dextrose, even after dialysis, probably makes the sol very stable. They also obtained a purple colour by depositing the colloid in stannic hydroxide. E. Fouard obtained colloidal tellurium by electrolyzing a soln. of a salt of the metal containing a pure organic colloid (albumin, starch, or gelatin) with a current of a few milliampères. At the cathode the metal ions are neutralized by the repelled negatively-charged colloid micelles. A colloidal organo-metallic complex is thus formed. The anode is separated by immersion in a collodion cell rendered semi-permeable by precipitated copper ferrocyanide. The cathode should be a bad conductor, so as to reduce the frequency with which formation of the complex occurs on the cathode. The flocculation of the colloidal soln. by boiling or by the addition of electrolytes was studied by A. Gutbier, C. Paal and C. Koch, W. Biltz, J. J. Doolan, etc. S. Utzino observed that the maximum stability of colloidal tellurium ground in the so-called colloid mill, is not necessarily obtained with the finest subdivision. R. Auerbach studied the coloured soln. of tellurium in sulphuric acid—*vide infra*, oxysulphates. A. Gutbier and B. Ottenstein said that the colloidal particles are negatively charged. W. Reinders discussed the distribution of the colloid between two liquid solvents.

References.

[1] A. T. von. Gersdorff and W. L. Kölreuter, *Trommsdorff's Journ.*, (2), **8**. 285, 1824; *Schweigger's Journ.*, **62**. 213, 1831; J. Farbaky, *Zeit. angew. Chem.*, **10**. 11, 1897; E. Donath, *ib.*, **3**. 216, 1896; F. M. Horn, *ib.*, **1**. 159, 1888; J. Löwe, *Sitzber. Akad. Wien*, **10**. 727, 1853; *Journ. prakt. Chem.*, (1), **60**. 163, 1853; A. Oppenheim, *ib.*, (1), **81**. 308, 1860; *Beobachtungen über des Tellur und einige seiner Verbindungen*, Göttingen, 1857; M. H. Klaproth, *Crell's Ann.*, **1**. 91, 1798; *Gilbert's Ann.*, **12**. 246, 1802; *Beiträge zur chemischen Kenntniss der Mineralkörper*, Berlin, **3**. 1, 1802; London, **2**. 1, 1804; A. von Schrötter, *Sitzber. Akad. Wien*, **66**. 79, 1872; *Ber.*, **6**. 552, 1873; E. Priwoznik, *Vorkommen von Tellur und Gewinnung aus seinen Erzen*, Wien, 1893; *Osterr. Zeit. Berg. Hütt.*, **45**. 219, 1895; A. Haush, *ib.*, **24**. 234, 1876; H. Schnitzler, *Dingler's Journ.*, **211**. 484, 492, 1874; H. Schwarz, *ib.*, **186**. 29, 1867; K. B. Heberlein, *Beiträge zur Kenntniss des Tellurs*, Basel, 1898; *Berg. Hütt. Ztg.*, **54**. 41, 1895; F. Becker, *Sitzber. Phys. Med. Soc. Erlangen*, **8**. 23, 1876; *Liebig's Ann.*, **180**. 257, 1876; P. Köthner, *ib.*, **319**. 1, 1901; *Das reine Tellur und sein Atomgewicht*, Halle a. S., 1901; A. Schuller, *Ber. Ungarn Naturwiss.*, **1**. 64, 1884; *Wied. Ann.*, **18**. 320, 1883; J. J. Berzelius, *Schweigger's Journ.*, **6**. 311, 1812; **34**. 78, 1823; *Pogg. Ann.*, **8**. 411, 1826; **28**. 392, 1833; **32**. 1, 577, 1834; H. Hess, *ib.*, **28**. 407, 1833; F. Wöhler, *ib.*, **11**. 161, 1827; W. Pethybridge, *U.S. Pat. No.* 700037, 700038, 1903; *Zeit. Elektrochem.*, **9**. 213, 1903; *Brit. Pat. No.* 1738, 4375, 1901; A. Wehrle, *Zeit. Phys. Math.*, (2), **9**. 133, 144, 1831; (2), **3**. 317, 1835; *Isis*, 357, 1833; *Pogg. Ann.*, **21**. 599, 1831; *Schweigger's Journ.*, **59**. 482, 1830; E. Matthey, *Proc. Roy. Soc.*, **68**. 161, 1901; F. D. Crane, *Amer. Chem. Journ.*, **23**. 408, 1900; J. F. Norris, H. Fay and D. W. Edgerly, *ib.*, **23**. 105, 1900; F. Krafft and R. E. Lyons, *Ber.*, **27**. 1769, 1894; F. Krafft and L. Merz, *ib.*, **36**. 4344, 1903; O. Steiner, *ib.*, **34**. 570, 1901; G. Pellini, *ib.*, **34**. 3807, 1901; L. Staudenmaier, *Zeit. anorg. Chem.*, **10**. 189, 1896; G. W. A. Kahlbaum, K. Roth, and P. Siedler, *ib.*, **29**. 177, 1902; A. Gutbier, *ib.*, **32**. 31, 1902; *Studien über das Tellur*, Leipzig, 1901; R. Schelle, *Proc. Internat. Congress Appl. Chem.*, **7**. iii, 80, 1909; C. Himly, *Schriften Naturwiss. Kiel*, 117, 1877; H. Rose, *Zeit. anal. Chem.*, **1**. 73, 1862; *Handbuch der analytischen Chemie*, Braunschweig, **2**. 449, 474, 1871; C. Alexi, *Ueber die Bestimmung von Selen und Tellur und die Untersuchung von selen- und tellurhaltigen Handelskupfer*, Berlin, 1905; P. Hulot, *Bull. Soc. Chim.*, (4), **27**. 33, 1920; (4), **29**. 1070, 1921; C. Whitehead,

Journ. Amer. Chem. Soc., **17**. 849, 1895 ; E. Keller, *ib.*, **19**. 771, 1897 ; **22**. 241, 1900 ; V. Lenher, *ib.*, **21**. 347, 1899 ; **24**. 355, 1902 ; F. Stolba, *Casopsis Crumysl Chem.*, **2**. 12, 65, 390, 1893 ; *Dingler's Journ.*, **198**. 262, 1870 ; *Sitzber. Ges. Prag.*, 325, 1873 ; P. Berthier, *Ann. Chim. Phys.*, (2), **51**. 156, 1832 ; D. Klein and L. Morel, *ib.*, (6), **5**. 81, 1885 ; L. Kastner, *Zeit. anal. Chem.*, **14**. 142, 1885 ; C. M. Dyson, *Chem. Age*, **19**. 17, 1928 ; R. W. E. MacIvor, *Chem. News*, **86**. 308, 1902 ; M. Shimose, *ib.*, **49**. 26, 1884 ; E. Divers and M. Shimose, *ib.*, **51**. 199, 1885 ; *Journ. Chem. Soc.*, **47**. 439, 1885 ; B. Brauner, *ib.*, **55**. 382, 1889 ; *Monatsh.*, **10**. 413, 1889 ; *Sitzber. Akad. Wien*, **98**. 456, 1889 ; F. C. Mathers and H. L. Turner, *Trans. Amer. Electrochem. Soc.*, **54**. 293, 1928.

[2] A. Gutbier, *Studien über das Tellur*, Leipzig, 1901 ; *Zeit. anorg. Chem.*, **32**. 51, 91, 1902 ; **42**. 177, 1904 ; A. Gutbier and F. Resenscheck, *ib.*, **40**. 264, 1904 ; A. Gutbier and B. Ottenstein, *ib.*, **149**. 223, 1925 ; **160**. 48, 1927 ; A. Gutbier, J. Haber, and P. Eckert, *Koll. Zeit.*, **32**. 329, 1923 ; C. Paal and C. Koch, *Ber.*, **38**. 536, 1905 ; L. Lilienfeld, *Brit. Pat. No.* 173507, 1921 ; E. Fouard, *Compt. Rend.*, **184**. 328, 1927 ; E. Müller and R. Lucas, *Zeit. Elektrochem.*, **11**. 521, 1905 ; W. Reinders, *Koll. Zeit.*, **13**. 255, 1913 ; *Proc. Acad. Amsterdam*, **16**. 379, 1913 ; J. J. Doolan, *Journ. Phys. Chem.*, **29**. 178, 1925 ; G. Bredig, *Anorganische Fermente*, Leipzig, 1901 ; C. Levaditi, *French Pat. No.* 626506, 1926 ; P. P. von Weimarn and B. V. Maljisheff, *Journ. Russ. Phys. Chem. Soc.*, **42**. 484, 1910 ; P. P. von Weimarn, *ib.*, **42**. 476, 1910 ; W. Biltz, *Gött. Nachr.*, 1, 1904 ; S. Utzino, *Japan Chem. Journ.*, **2**. 21, 1925 ; *Koll. Zeit.*, **32**. 149, 1923 ; R. Auerbach, *ib.*, **38**. 343, 1926 ; *Zeit. Phys. Chem.*, **121**. 337, 1926 ; J. J. Berzelius, *Pogg. Ann.*, **8**. 411, 1826 ; **28**. 392, 1833 ; **32**. 1, 577, 1834 ; *Schweigger's Journ.*, **6**. 311, 1812 ; **34**. 78, 1823 ; B. Brauner, *Monatsh.*, **9**. 414, 1889 ; *Journ. Chem. Soc.*, **55**. 382, 1889.

§ 3. The Physical Properties of Tellurium

J. J. Berzelius[1] described tellurium cooled from the molten state, as a tin-white crystalline mass with a metallic lustre, and added that it is brittle and easily powdered ; and R. Schelle added that after fusion tellurium is silver-white, and if fused in sodium hydrosulphate, and cooled in carbon dioxide, a crystalline star resembling that of antimony is formed. A. W. Wright said that a thin film is dull purple ; and D. Gernez, that the vapour is golden-yellow or orange-yellow. G. Magnus said that tellurium usually occurs massive—columnar or granular—dark grey or black in colour. J. C. L. Schröder van der Kolk said that the streak of tellurium is reddish violet-grey. When precipitated by the action of air on a dil. soln. of potassium telluride, by the addition of water to a conc. sulphuric acid soln., or by the action of sulphur dioxide on a soln. of a tellurite, it furnishes a brown powder. N. W. Fischer observed that the tellurium precipitated by metals—*e.g.* zinc, tin, iron, etc.—from a soln. of tellurium dioxide in hydrochloric acid as a black powder, which has a metallic lustre when rubbed with a burnishing tool ; if precipitated by lead, the tellurium is dendritic. D. Beljankin said that tellurium precipitated from alkaline soln. consists of microscopic rhombohedra. L. P. Sieg said that a film of spluttered tellurium probably consists of crystals few or many in number. W. Phillips made some observations on the natural crystals, and G. Rose showed that the natural crystals are trigonal with the axial ratios $a : c = 1 : 1{\cdot}3298$; and observations were made by A. Breithaupt, F. A. Genth, L. Tokody, G. vom Rath, A. des Cloizeaux, J. Loczka, H. von Foullon, and G. Rolland. C. Haushofer, and F. Fouqué and A. Michel-Lévy, described the sublimed crystals as rhombohedra, and G. W. A. Kahlbaum, as hexagonal prisms. G. Rose, and C. W. Zenger said that the crystals obtained by freezing the molten metal are rhombohedra. J. Margottet gave $a : c = 1 : 1{\cdot}33595$ for the axial ratio of the artificial crystals. G. Rose represented the hexagonal prisms of the natural crystals by Fig. 1, and the crystals may also be acicular and those obtained from soln. of potassium or ammonium telluride are also needle-like, Fig. 2.

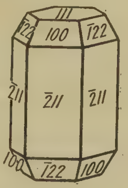

FIG. 1.—Natural Crystal.

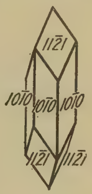

FIG. 2.—Crystal precipitated from Potassium Telluride.

The crystals show signs of twinning. The ($\bar{2}11$)-cleavage is complete, and the

(111) cleavage is incomplete. L. P. Sieg found that a spluttered tungsten film has a crystalline structure. The **X-radiograms** obtained by A. J. Bradley corresponded with crystals having a space-lattice with a simple trigonal structure having inter-axial angles almost 90° in which each atom is slightly displaced towards two of the six adjacent atoms. This furnishes a threefold spiral composed of three inter-penetrating simple triangular lattices—*vide* selenium. M. K. Slattery found that both elements crystallize in a simple triangular lattice with 3 atoms associated with each point of the lattice. The side *a* of the basal triangle is 4·44 A.; the height, *h*, is 5·912 A.; the axial ratio, *c*, 1·33, and the density, 6·25. The arrangement of the atoms in the space-lattice about the prism edge, *h*, forms an ascending helix, with a threefold symmetry, so that each atom is exactly above the third atom below in the same helix. The X-radiogram does not distinguish between a right- and left-handed screw. The prisms edge is thus a screw-axis; and the interactions of the screw-axis with the basal plan, form the unit basal triangles. The radius of the helix is 1·20 A., so that this represents the distance from the centre of each atom to the axis of the helix. The shortest distance between the atoms in the same helix, 2·86 A., is less than 3·46 A., the shortest distance between atoms in different helices. This means that the atoms in the same helix are held together by cohesive forces much greater than those binding atoms in different helices, and that the crystal is harder in the direction of the screw axis than perpendicular to it. The uniqueness of this axis was emphasized by A. J. Bradley, and R. F. Mehl and B. J. Mair, who showed that it accounts for many of the directional properties of the two elements, and that crystallization is probably preferential along this line. This was shown to be the case by P. W. Bridgman, who found that the trigonal or screw axis lies longitudinally in the casting—*vide infra*. S. von Olshausen, and G. Wassermann made some observations on this subject; the data were also summarized by P. P. Ewald and C. Hausmann. W. Hume-Rothery studied the lattice-constants of the elements.

It is not probable that **isomorphism** exists between tellurium and arsenic, antimony, and bismuth; but tellurium is isomorphous with the trigonal form of selenium. The isomorphism with selenium was discussed by G. Rose, C. F. Rammelsberg, P. Groth, W. Muthmann, etc. J. W. Retgers studied the isomorphism of sulphur, selenium, and tellurium, and concluded that while sulphur and selenium showed complete crystal similarity, tellurium was isomorphous with neither element. No isomorphous mixtures are formed between potassium tellurate on the one hand, and with potassium sulphate, selenate, chromate, molybdate, tungstate, manganate, or ferrate on the other hand. Nor could J. F. Norris and W. A. Kingman prepare isomorphous hydroselenates and hydrotellurates. The only case of isomorphism known to J. W. Retgers was that between the sulphides, selenides, and tellurides, which crystallize in the cubic system, but he argued that the crystals in this system have such a high degree of crystallographic symmetry that their power to form mixed crystals is not a satisfactory proof of true isomorphism. Potassium tellurate is not isomorphous with the selenate, but it is isomorphous with the osmiate. This with the atomic weight of tellurium has been used as an argument for placing tellurium in the eighth group. The isomorphism of compounds of the type K_2TeBr_6—where bromine may be replaced by chlorine, and potassium by ammonium, rubidium, or cæsium—observed by H. L. Wheeler, and W. Muthmann with the corresponding selenium compound and with the analogous platinum salt, is also a result of all crystallizing in the cubic system. J. F. Norris and R. Mommers found that the double bromide of platinum and dimethylamine, crystallizing in the orthorhombic system, is isomorphous with the analogous compounds of selenium and tellurium, and this case of isomorphism is not open to the objections raised by J. W. Retgers; and similar remarks apply to the isodimorphism of G. Pellini's diphenyl dibromotelluride, $(C_6H_5)_2TeBr_2$. F. Krafft and O. Steiner discussed the mutual replacement of sulphur, selenium, and tellurium in this family of elements. G. Pellini and G. Vio, and Y. Kimata found that the f.p. curve of mixtures of selenium and tellurium show that solid soln. are formed in agreement with the isomorphism of the trigonal forms of these two elements—*vide* tellurium selenide in the preceding chapter. G. Pellini also came to a similar conclusion with respect to sulphur. Some of the isomorphous crystals have the form of rhombic sulphur. A similar conclusion was drawn by E. Billows. The structure of the crystals of tellurium was discussed by V. M. Goldschmidt.

From the **vapour density** at 2100°, H. von Wartenberg found the **molecular weight** to be 160. E. Moles found the mol. wt. deduced from the f.p. and conductivity of soln. in sulphuric acid to be abnormal. A. Jouniaux inferred that tellurium is monatomic at 357° and more complex at lower temp.; it is diatomic at about 1500°. For the mol. wt. in iodine soln., *vide infra*, tellurium halides. R. Auerbach's cryoscopic observations showed that tellurium dissolves as Te in pyrosulphuric acid. The **specific gravity** of native tellurium varies with its degree of purity. Thus, J. Loczka gave 6·084; R. W. E. MacIvor, 6·2; V. R. von Zepharovich, 5·86; and F. A. Genth, 6·275. For the artificial crystals M. H. Klaproth gave 6·115; F. J. Müller von Reichenstein, 6·393; J. Löwe, 6·180; E. Matthey for 98·7 per cent. Te, 6·27; G. Magnus, 6·1379; and D. Klein and L. Morel, 6·204–6·215. J. J. Berzelius gave 6·245 for the average of five determinations of crystals obtained from the molten element, but preferred the higher value 6·258 because of pores. E. Priwoznik gave 6·2459 at 18·2° for a sample which had been melted in hydrogen, and C. F. Rammelsberg, 6·38 to 6·42; D. Beljankin gave 6·338 at 18°–22°; and H. Fay and C. B. Gillson, 6·243. For distilled tellurium, V. Lenher and J. L. R. Morgan gave 6·194 to 6·204—mean 6·199, and G. W. A. Kahlbaum, 6·23538 at 20°. D. Beljankin gave 6·157 for the sp. gr. of tellurium precipitated from alkaline soln.; and 6·015 at 20° for amorphous precipitated tellurium. C. F. Rammelsberg gave 5·93 for the sp. gr. of the amorphous tellurium precipitated by sulphur dioxide; he added that the amorphous tellurium suffers no change if heated to 300°. W. Spring gave for tellurium which had been subjected to high compression, as well as for the element which had not been compressed:

		0°	20°	40°	60°	80°	100°
Sp. gr.	Not compressed	6·2322	6·2194	6·2052	6·1500	6·1366	6·0640
	Compressed .	6·2549	6·2419	6·2294	6·2170	6·3030	6·1891

M. L. Huggins calculated for the **atomic radius,** 2·46 A.; J. C. Slater, 1·22 A.; and W. F. de Jong and H. W. V. Williams, 1·33 A. W. L. Bragg calculated 1·33 A. for the at. radius; A. Ferrari, 3·025 A. E. T. Wherry gave 0·81 to 0·89 A. for quadrivalent tellurium, and 0·56 A. for sexivalent tellurium. F. H. Burstall and S. Sugden discussed the parachor of some bivalent tellurium compounds.

V. Lenher and co-workers said that the metal expanded slightly after solidification. E. Cohen and J. F. Kröner[2] observed that the treatment to which tellurium has been subjected greatly influences the sp. gr., and it varies between 6·272 and 5·949. Tellurium, prepared by the reduction of telluric acid by hydrazine sulphate, had a sp. gr. of 3·242. This low value was traced to occluded nitrogen. They assume that tellurium exists in two forms present as **dynamic allotropes** in equilibrium α–Te$\rightleftharpoons\beta$–Te. The variety with the smaller sp. gr. is stable at the higher temp. Thus, the sp. gr. of a sample before heating to 350° was 6·233, and after heating to this temp., 6·203. A. Damiens said that observations on the sp. gr. of tellurium purified by distillation in vacuo, and either sublimed, or slowly cooled from the molten state, lend no support to E. Cohen and J. F. Kröner's theory of dynamic allotropy. Sublimed tellurium of sp. gr. 6·310 is not changed by prolonged heating at various temp. Tellurium prepared in other ways may appear to have a smaller sp. gr. owing to its porosity. Amorphous tellurium, of sp. gr. 5·85 to 5·87, is transformed by heat into crystalline tellurium, and heat is evolved during the transformation. W. Haken reported that the electrical conductivity indicated the existence of two allotropic forms with a transition temp. at 354°; but A. Damiens inferred from observations on the sp. gr., rate of cooling and heating, sp. ht. and heat of reaction, that the analogy between the **allotropy** of sulphur and tellurium does not apply since tellurium is characterized by the existence of a single crystalline form. Attempts by H. Staudinger and W. Kreis to prepare solid red tellurium by cooling the vapour at 1000° in liquid air were unsuccessful. C. del Fresno, and I. I. Saslavsky studied the at. vol. of tellurium in its compounds. L. S. Ramsdell calculated 1·27 A. for the atomic radius ; H. G. Grimm made observations on this subject.

M. Toepler [3] observed an irregularity in the vol. changes of tellurium as it cools from the molten state, and this he attributed to the formation of an amorphous plastic variety of tellurium just before it solidifies. J. R. Rydberg gave 2·3 for the **hardness** of tellurium (diamond 10). P. Saldau gave 18·43 kgrms. per sq. mm. for the hardness of tellurium when that of lead is 3·92 kgrms. per sq. mm. E. Schmid and G. Wassermann discussed the percussion figures of the crystals, and also the plastic deformation. P. W. Bridgman found the cubic **compressibility** to be 0·0000024 kgrm. per sq. cm.; **Poisson's ratio,** 0·33 ; the **tensile strength** expressed as a breaking load in tension was 115 kgrms. per sq. cm. A piece of tellurium wire 8 cms. long and 0·0348 cm. diameter, fastened rigidly at one end, and bent by a weight at the other, showed a maximum permanent set of 0·11 cm., and broke under a deflection of 1·82 cm. The brittleness is extreme for a metal, but is not as high as for glass. P. W. Bridgman measured the **elastic constants ;** he found the initial linear compressibility, p in kgrms. per sq. cm., for angle crystals to be, at 30°, $-4{\cdot}14\times10^{-7}$ when parallel, and $27{\cdot}48\times10^{-7}$ when vertical to the trigonal axis ; at 30°, when perpendicular to the trigonal axis $-\delta l/l=27{\cdot}48\times10^{-7}p-52{\cdot}7\times10^{-12}p^2$ at 30°, and at 75°, $27{\cdot}7\times10^{-7}p-53{\cdot}6\times10^{-2}$ at 75° ; at 75°, when parallel to the trigonal axis, $+\delta l/l=4{\cdot}137\times10^{-7}p-9{\cdot}6\times10^{-12}p^2$, and at 75°, $5{\cdot}132\times10^{-7}p-13{\cdot}2\times10^{-12}p^2$. The remarkable fact is that the compressibility along the trigonal axis is negative, so that when the crystal is subjected to hydrostatic press. all over, it elongates along the trigonal axis. The cubic compressibility is normal $-\delta v/v_0=50{\cdot}82\times10^{-7}p-101{\cdot}1\times10^{-12}p^2$ at 30°, and $50{\cdot}41\times10^{-7}p-85{\cdot}6\times10^{-12}p^2$ at 75°. The cubic compressibility thus decreases with rise of temp. R. F. Mehl and B. J. Mair explain this as follows :

> It is evident that this crystal structure is not closely packed, and it is conceivable that a change in either of the major dimensions, that of the side of the unit basal triangle, a, or that of the prism edge, h, should cause a change in density resulting merely from a difference in the closeness of the packing of the atoms, the two inter-atomic distances remaining unchanged. In such a process a lengthening of the prism edge, h, would cause a shortening of a and also a shortening of the radius of the helix. If such an elongation would result in an increase in density, it is entirely reasonable to suppose that an increase in press. tending towards an increase in density, would in fact cause a lengthening of this axis, with an attendant shortening of the other two dimensions. Such a lengthening would obviously cause the abnormal coeff. observed by P. W. Bridgman. Fig. 3 shows a curve representing density as a function of the height of the unit prism. The values from which the curve was plotted were calculated by taking a series of values for h and keeping the inter-atomic distances, 2·86 A. and 3·46 A., unchanged, calculating the radius of the helix and the side of the unit basal triangle, a, and from these the density of the hypothetical crystal. The curve passes through a minimum at a density slightly greater than 6·20, corresponding to a value for h of 5·55 A. For a prism of height less than 5·55 A. an increase in press. tending to cause an increase in density could do so only by shortening h, the two interatomic distances remaining unchanged, and the screw-axis would therefore show the usual positive compressibility coeff. On the other hand, if the value for h lay to the right of 5·55 A. an increase in press. would cause a lengthening in h, since such a process would result in an increase in density. The actual value of h for tellurium, indicated by the arrow in the

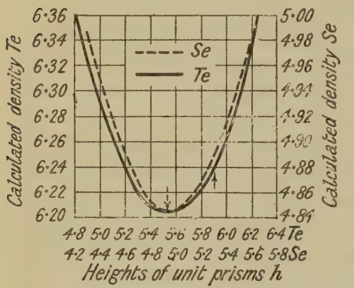

FIG. 3.—Calculated Densities of Tellurium and Selenium with Space-Lattices of Different Heights.

figure, is 5·91 A. and is therefore to the right of the minimum, so that an increase in press. should cause an increase in h, or, in other words, a negative compressibility coeff. along this axis.

Measurements have not been made with selenium, but R. F. Mehl and B. J. Mair, applying the same argument, state:

> The actual value for h, indicated by the arrow, dotted line, Fig. 3, appears to lie very slightly to the left of the minimum, and therefore, the height of the unit prism would very likely decrease with the application of press. (assuming, of course, that the lattice dimensions used in the calculations are correct); but since the screw-axis is in a state of greater compression than the triangular axes the compressibility along this axis is probably low. Resisting the elongation (or contraction) of the helix upon the application of press., there is the tendency within the lattice to maintain the angle formed by any three atoms in the same helix at (for tellurium) 126·5°, and this tendency doubtless becomes more and more urgent as the angle departs further and further from this value, so that it may be assumed that the adjustment of density by the lengthening or shortening of the helix meets with increasing resistance as the press. rises. It is this restraint which prevents the helix from straightening completely upon the first application of press.

H. Fizeau gave $\alpha=0{\cdot}00001675$ for the coeff. of **thermal expansion**—linear—between 0° and 40°; and 0·00001732 between 0° and 50°; whilst W. Spring gave for coeff. of cubical expansion $0{\cdot}0_43440$ between 0° and 20°; $0{\cdot}0_43737$ between 0° and 60°; and $0{\cdot}0_43687$ between 0° and 100°. P. W. Bridgman gave for the linear thermal expansion at 20°—$1{\cdot}6\times10^{-6}$ when parallel and $27{\cdot}2\times10^{-6}$ when perpendicular to the trigonal axis. E. Jannetaz found that the ratio of the sq. root of the **thermal conductivity,** k_γ, in the direction of the principal axis, and k_a, in the direction of the base, is $(k_a/k_\gamma)^{\frac{1}{2}}=0{\cdot}81$. H. Kopp gave 0·0475 for the **specific heat;** H. V. Regnault, 0·0474 for distilled tellurium, and 0·0516 for that precipitated by sulphur dioxide; M. Berthelot and C. Fabre gave 0·0483 for fused tellurium slowly cooled, 0·0524 for that precipitated by sulphur dioxide, and 0·0518 for that distilled in a current of sulphur dioxide; A. Wigand, for crystalline tellurium between 15° and 100°, gave 0·0483, and for amorphous tellurium, 0·0525; and G. W. A. Kahlbaum and co-workers, 0·04878 for that distilled in vacuo. W. A. Tilden gave 0·0469 between —182° and 15°; 0·0483, between —15° and 100°; 0·0487, between —15° and 200°; and 0·0500, between —15° and 380°. J. Dewar gave 0·0288 between —253° and —196°. The corresponding **atomic heats** are 3·68 between —253° and —196°; 5·98 between —182° and 15°; 6·16 between 15° and 100°; and 6·38 between 15° and 380°. E. Adinolefi[4] found that the sp. ht. of tellurium is increased by about 8 per cent. after exposure to the X-rays, and this is attributed to a change in the structure of the element. The relations of the sp. ht. were studied by I. Maydel.

T. Carnelley and W. C. Williams found the **melting point** of tellurium to be between 452° and 455°; R. Pictet, 525°; H. Fay and co-workers, and S. Umino, 446°; K. Mönkemeyer, 428°; W. Guertler and M. Pirani, 450°; H. Pélabon, 452°; W. R. Mott, 452°; W. Biltz and W. Mecklenburg, 455°; M. Chikashige, 438°; M. Kobayashi, 437°; and E. Matthey, for 97·0 per cent. Te, 450°. A. Damiens gave 453° for the m.p., and observed no break in the heating or cooling curve between this temp. and the ordinary temp. W. Guertler and M. Pirani gave 450° for the best representative value. A. Simek and B. Stehlik gave 452° for the m.p. in vacuo; in hydrogen, the m.p. is lowered 0·15°, and in carbon dioxide 0·2°. There is a marked contraction during the freezing of the mother-liquid, and with slow cooling, a cavity is formed in the middle of the mass; and if quickly cooled, the surface freezes first, and numerous small cavities form in the interior. If tellurium be melted in a glass vessel, the glass is inclined to shatter on cooling owing to the formation of pores between the crystals producing an apparent expansion. H. Carlsohn found that the m.p. of tellurium compounds does not follow the additive rule. J. J. Berzelius said that tellurium boils at a temp. higher than the softening temp. of glass, and it is converted into a yellow vapour, the colour of chlorine. M. H. Klaproth added that when heated to redness in a retort, the tellurium sublimes into the neck in the form of shining drops. F. Wöhler, and A. Oppenheim distilled the element in a porcelain retort at a red-heat, J. J. Berzelius distilled it in a current of hydrogen; and A. Schuller obtained well-defined crystals by distillation in vacuo. L. Staudenmaier observed that a little volatilization occurs at 300°; H. St. C. Deville and L. Troost gave 1390° for the **boiling point**; and W. R. Mott, 1390°; while F. Krafft and L. Merz added that in the vacuum of a cathode light marked sublimation occurs at 430°, and the b.p. at 58 mm. press. is 478°. J. Joly observed that sublimation of tellurium dioxide occurs at 850° with native tellurium, and at 700° with purified tellurium; and of the monoxide, respectively at 525°, and 470°. J. J. Doolan and J. R. Partington found the **vapour pressure** of tellurium to be 0·0186 atm. at 671°; 0·00440 at 578°; and 0·000610 at 488°. The corresponding latent **heat of volatilization** is 24·7 Cals. per mol. between 578° and 671°, and 28·2 Cals. per mol. between 488° and 578°—assuming the diatomic Te_2-molecule. The mean value is 26·5 Cals. per mol. H. Biltz obtained a **vapour density** of 9·13 at 1880° corresponding with the Te_2-molecule. He added that H. St. C. Deville and L. Troost's determinations are inaccurate. H. Pélabon calculated the latent **heat of fusion** to be 20 to 21 Cals. per mol. W. Herz gave 7·4 Cals. per gram; and S. Umino, 33·5 cals. per mol. J. J. van Laar discussed the equation of state of the solid.

M. Berthelot and C. Fabre found the **heat of solution** of tellurium in bromine and bromine water is 66·7 Cals. in the case of crystalline tellurium; 42·6 Cals. in the case of tellurium precipitated by sulphur dioxide; 66·7 Cals. for tellurium precipitated by oxygen from potassium telluride; and 67·0 Cals. for tellurium separated by oxygen from hydrogen telluride. Tellurium separated from ferric chloride by hydrogen telluride is crystalline. Tellurium rapidly cooled from the molten state develops 41·4 to 58·1 Cals. indicating that it is an indefinite mixture of amorphous and crystalline tellurium. The calculated **heat of crystallization** from amorphous selenium is thus 12·096 cals. for 64 grms., but A. Damiens obtained 2·63 cals. for this constant. S. Umino gave 0·63 cal. per mol. for the **heat of transformation** at 348°. G. N. Lewis and co-workers gave 12·8 for the **entropy** of tellurium at 25°, and B. Bruzs, 17·2 at the m.p. E. Kordes calculated 1·63 for the ratio $Q_{\text{cals.}}/T$ for Te, and 6·52 for Te_4. W. Herz studied the subject. J. Franck calculated 69 Cals. for the work of dissociation of Te_2; and V. Kondrateeff, 65 Cals.

C. Cuthbertson and E. P. Metcalfe [5] found the **index of refraction** of tellurium vapour to be 1·002620 for $\lambda=546_{\mu\mu}$; 1·002495 for $\lambda=589{\cdot}3_{\mu\mu}$; and 1·002370 for $\lambda=656{\cdot}3_{\mu\mu}$. R. F. Miller found that the refractive indices for single crystals with the light parallel and perpendicular to the plane of incidence are, respectively, 1·9 and 1·7. The whole range of wave-length, L. P. Sieg and G. D. van Dyke gave 2·50 to 3·14 and 2·05 to 2·68 respectively when the light falling on one of the hexagonal faces is polarized with the electric vector respectively parallel and perpendicular to the principal crystal axis. The absorption constants are respectively 0·40 to 0·56, and 0·54 to 0·67. Observations were also made by A. H. Pfund, and E. O. Hulburt. W. W. Coblentz gave for the percentage **reflecting power,** R, of tellurium for rays of wave-length λ:

λ . .	0·6μ	0·8μ	1·0μ	2·0μ	4·0μ	7·0μ
R . .	49	48	50	52	57	68 per cent.

R. F. Miller found that the reflecting powers of single crystals with the crystal axis parallel and perpendicular to the plane of incidence respectively are 2·9 and 2·7 over the whole range of wave-lengths; L. P. Sieg and G. D. van Dyke gave 0·28 to 0·34 and 0·26 to 0·30 when the light falling on one of the hexagonal faces is polarized with the electric vector respectively parallel and perpendicular to the principal crystal axis. From observations on the halides and organic tellurium compounds, G. Pellini and A. Menin found the **atomic refraction** with the μ-formula to be 32·06–33·81, and with the μ^2-formula 15·28–16·66. J. E. Calthrop studied the relation between the at. vol., and the index of refraction. K. Spangenberg compared the mol.

refractions of the oxides, sulphides, selenides, and tellurides. M. A. Shirmann studied the polarization of light by submicroscopic particles of tellurium.

R. T. Simmler [6] observed that the **flame spectrum** of tellurium in a colourless gas-flame is continuous, and a similar result was obtained by G. Werther; A. Mitscherlich also observed that the spectrum of the vapour of tellurium in burning hydrogen is continuous. The flame spectrum of tellurium was also examined by G. Salet, W. N. Hartley, and J. M. Eder and E. Valenta. The **spark spectrum** of tellurium between electrodes of that element was observed by W. A. Miller, W. Huggins, R. J. Lang, H. Nagaoka and co-workers, L. and E. Block, A. M. Vieweg and co-workers, J. C. McLennan and A. C. Lewis, and T. R. Robinson. As in the case of sulphur, tellurium furnishes two spectra—the line, and the band spectra. The **line spectrum** of tellurium obtained by the gas discharge between tellurium electrodes was measured by R. Thalén, A. Ditte, G. Salet, R. Capron, G. L. Ciamician, W. N. Hartley, W. N. Hartley and W. F. Adeney, R. J. Lang, E. Demarçay, C. Runge and F. Paschen, A. de Gramont, F. Exner and E. Haschek, P. Köthner, P. G. Nutting, A. Hagenbach and H. Konen, E. Goldstein, and J. M. Eder and E. Valenta. The principal lines in the visible region are 6438 in the red, 6040·7, 6011·3, 5974, and 5936 in the orange-yellow; 5982, and 5756 in the yellow; 5707, and 5648 in the yellowish-green; 5575, 5489, 5478, 5448, 5367, 5311, 5218, 5153, and 5105 in the green; 4302, 4275, and 4260 in the indigo-blue; and 4221, 4062, 4055, 4006, 3984, and 3969 in the violet. W. L. Dudley and E. V. Jones found that the spark spectrum remained the same after the element had been fractionally precipitated by hydrazine hydrochloride twenty times. E. J. Allin studied the under-water spark spectrum. The **arc spectrum** was examined by F. Exner and E. Haschek, A. Hagenbach and H. Konen, H. S. Uhler and R. A. Patterson, M. Kimura, J. Stark and R. Küch, E. Gehrcke and O. von Baeyer, and J. M. Eder and E. Valenta. The **band spectrum** was obtained by G. Salet by passing a spark through the vapour of tellurium. D. Gernez obtained an **absorption spectrum,** extending from the yellow to the violet, by passing light through the vapour of tellurium in an atm. of carbon dioxide. The absorption spectrum was studied by A. W. Wright, J. J. Dobbie and A. J. Fox, J. C. McLennan and R. F. B. Cooley, B. Rosen, A. Michaelis, R. V. Zumstein, E. Rütten, C. H. Cartwright, and W. Friederichs; and the band spectrum, by R. Mecke. F. K. Bell examined the ultra-red absorption spectrum of organic sulphur compounds. The **reflection spectrum** was examined by J. Trowbridge and W. C. Sabine; the **cathode ray spectrum,** by P. Lewis; the **emission spectrum** of the vapour by E. Paterno and A. Mazzucchelli; and the resonance spectrum, by B. Rosen, who gave $\gamma=\alpha-250{\cdot}4n+0{\cdot}53n^2$, where α=23930, 25451 and 22411 respectively for the exciting mercury lines 4359 A., 4046 A., and 5461 A. The **ultra-violet spectrum** is particularly rich in lines. It was observed by F. Exner and E. Haschek, A. Grünwald, R. J. Lang, P. Lacroute, R. V. Zumstein, and V. Schumann. J. C. McLennan and co-workers, H. Schüler and H. Brück, E. V. Condon and G. H. Shortley, A. Porzeborsky, and R. C. Gibbs and A. M. Vieweg discussed the **structure** of the arc spectrum. R. J. Lang discussed the **series spectrum.**

According to W. Steubing,[7] the vapours of the four elements of the sulphur family show a marked **fluorescence** discussed in connection with selenium, and similarly also with the observations of D. Diestelmeier, H. R. Pogorzelska, and B. Rosen; J. C. McLennan and co-workers studied the fluorescence spectrum of tellurium vapour. H. R. Pogorzelska examined the banded fluorescence of the resonance spectrum of tellurium vapour. W. Steubing found that a magnetic field has no effect on the intensity of the resonance and fluorescent spectra. W. Kessel also studied the resonance spectrum; and A. Smekal, the **Raman effect.**

The K-series in the **X-ray spectrum** of tellurium was observed by F. C. Blake and W. Duane,[8] A. Leide, S. Björck, B. Walter, B. B. Ray, M. Siegbahn, K. Chamberlain and G. A. Lindsay, M. Siegbahn and E. Jönsson, and there occur the lines $0{\cdot}456\alpha,\alpha$; and $0{\cdot}404\beta,\beta$. The L-series was measured by D. Coster, Y. Nishina, A. Leide, B. B. Ray, E. Hjalmar, K. Chamberlain and G. A. Lindsay, S. Björck,

M. Lindsay, M. Siegbahn, and H. Hirata. They include $3{\cdot}29100\alpha_2\alpha^1$; $3{\cdot}28199\alpha\alpha$; $3{\cdot}06997\beta\beta$; $2{\cdot}877\beta_2\gamma$; $2{\cdot}70647\gamma_2\delta$; $3{\cdot}04004\beta_4\gamma$; and $3{\cdot}00133\beta_3\phi$. S. Björck, and Y. Nishina also measured the M-, N-, and O-series. W. Herz gave $2{\cdot}43\times10^{-12}$ for the **vibration frequency.**

H. Müller[9] observed that the exposure of tellurium to intense α-rays did not affect the induced **radioactivity.** N. Piltschikoff studied the Moser rays emitted by tellurium; and T. Pavolini, and R. S. Bartlett, the **photoelectric effect** of tellurium films. E. Rupp studied the absorption of slow electrons by tellurium. B. Rosen discussed the resonance potentials. G. Piccardi calculated 8·43 volts for the **ionization potential.** E. Rabinowitsch and E. Thilo studied the subject. J. Vrede found that tellurium is not a good **radio-detector.**

A. de la Rive[10] noticed that tellurium is electrified by rubbing it with wool; and P. E. Shaw and C. S. Jex said that the triboelectricity acquired with glass is negative. K. F. Herzfeld discussed the metallic conductivity of tellurium. P. W. Bridgman said that the electrical properties of tellurium are unusual and variable; it is seldom that two observers obtain the same numerical values for any of its properties. This is taken to mean that tellurium under ordinary conditions contains two modifications in unstable equilibrium, and the proportions of the two forms change greatly with the manner of treatment—thus, the temp. coeff. of the same piece may be positive or negative according to its treatment. A. Matthiessen said that the **electrical conductivity** is such that if silver at 0° be 100, that of tellurium is 0·000777 at 19·6°. This works out at about 0·000466 mho at 19·6° (silver 60×10^{-4}), or roughly an **electrical resistance** of 2000 ohms. P. W. Bridgman gave for the sp. resistance of simple crystals at 20°, 56,000 ohms when parallel and 154,000 ohms when vertical to the chief axis. A. Matthiessen and M. von Bose added that when heated, the resistance increases with temp. up to 70°–80°. A. Schulze gave 2·1 for the ratio of the resistance in the solid and liquid state; A. Günther-Schulze made some observations on this subject. F. Exner said that at 20° the conductivity is 0·00293 if the element has been rapidly cooled, and, if slowly cooled, 0·00437. He found that the resistance R, arbitrary units, of a rod was:

	20°	50°	101°	180°	290°	182°	100°	51°	22°
R . .	7·07	7·86	8·10	5·25	4·40	5·21	14·75	31·1	40·0

The detailed results are plotted in Fig. 4. The resistance increases as the temp. rises to about 140°, and then falls up to 200°; as the temp. falls from 200°, the resistance increases steadily so that at ordinary temp. it is nine times as great as it was at 200°, and four to six times as great as it was initially at ordinary temp. On repeating the experiment the maximum no longer appears, but the resistance steadily decreases from the lowest to the highest temp. The more rapidly the sample is cooled, the smaller the final resistance, and conversely. The explanation is attributed to the better development of the crystals with slow cooling. E. Matthey found the resistance of a sample of 97 per cent. tellurium to be about 800 times as great as that of copper. For the ratio of the resistance R at $\theta°$ and R_2 at 0°, H. K. Onnes and B. Beckman found a minimum at −225°:

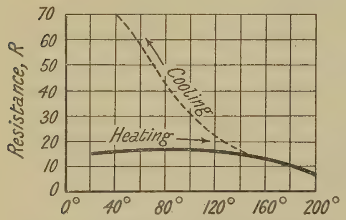

FIG. 4.—The Electrical Resistance of Tellurium (Heating and Cooling).

	−80°	−100°	−140°	−180°	−220°	−225°	−240°	−258·6°
R/R_0 .	0·773	0·732	0·659	0·596	0·547	0·546	0·568	0·624

H. Perlitz studied the relation between the space-lattice and the change of resistance with fusion; and R. Schuhmann found no difference in the e.m.f. of cells with amorphous and crystalline tellurium. V. Lenher and J. L. R. Morgan, A. Matthiessen, F. W. Warburton, F. Exner, W. G. Adams, and A. Guntz and W. Broniewsky, showed that the *structure* has a great influence on the resistance; they found that the sp. resistance of tellurium varied from 279 to 1152 ohms. A. Guntz and W. Broniewsky found that the sp. resistance of tellurium at 2° is 0·102 ohm, and, increasing with temp., attains a maximum at about 50°. It then diminishes until the m.p. is reached, Fig. 5; and added that, in agreement with F. Exner, the abnormal variation is due to the separation of crystals of varying sizes, and not to the formation of an allotropic modification of tellurium as was supposed by E. Cohen and J. F. Kröner. For J. M. Riviere's observations, *vide infra*, silver telluride. B. Beckman found the sp. resistance varied from 0·0493 to 0·617 ohm per cm. cube, and the *pressure* coeff. varied linearly from $-9\cdot1\times10^{-5}$ to $-26\cdot6\times10^{-5}$. P. W. Bridgman obtained a resistance of 0·00645 ohm per cm. cube; and a press. coeff. of —0·00012; and the average temp. coeff. from 0° to 24° was —0·0063. W. G. Adams said that the conductivity of tellurium is slightly increased by *exposure to light*, but not to the same extent as that of selenium. T. W. Case found that tellurium has a resistance less than a megohm, and does not change its resistance on exposure to light. R. S. Bartlett observed that tellurium shows a photoelectric effect at ordinary temp., and a 70 per cent. greater effect at —185°. P. Kapitza studied the change of the resistance in a magnetic field. L. Amaduzzi and M. Padoa found that isomorphous mixtures of selenium and tellurium show photoelectric sensibilities—ratio of the conductivity in darkness and in light—such that with 0·887 to 10·081 at. per cent. Te, the curve falls rapidly at first and then slowly with increasing tellurium content.

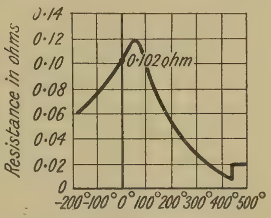

Fig. 5.—The Variation of the Electrical Resistance of Tellurium with Temperature.

C. A. Kraus and E. W. Johnson gave for the sp. resistance, R, of tellurium:

	480·5°	466·0°	449·1°	431·8°	404·7°	380·5°	363°
$R\times10^3$.	0·488	0·525	0·579	0·663	11·69	13·31	14·81
	Liquid				Solid		

and for the resistance at 440° of mixtures of tellurium and sulphur:

S .	0·0	5·0	30·0	50·0	70·0	75·0	77·5	80·0	85·0 per cent.
R .	$0\cdot0_36410$	$0\cdot0_38910$	0·2390	15·71	1870	10,920	33·650	114,500	231,700

B. Lange and W. Heller studied the **thermoelectric force** of the tellurium-platinum couple between —75° and 90°, and found that the thermoelectric force is almost constant, but it increases linearly from 0° to 40°, and nearly linearly up to 400°. A. Teichmann also measured the thermoelectric force of this couple. W. Ogawa also found the e.m.f. of the thermocouple with copper and tellurium to be -1000μ volts, and the current passes from tellurium to the copper at the hot junction.

M. A. Levitsky and M. A. Lukomsky found that the bismuth-tellurium couple gives a current of 360 microvolts per degree or three times that of the iron-constantan couple.

A. von Ettinghausen observed the change in the resistance of tellurium when exposed to a *magnetic field*; C. W. Heaps found that for small magnetic fields, of strength H, the effect on the resistance, R is $dR/R=100\cdot0\times10^{-12}H^2$ for transverse fields, and $dR/R=27\cdot7\times10^{-12}H^2$ for longitudinal fields. The subject was studied by P. Kapitza. According to P. I. Wold, the change of resistance in the magnetic field is proportional to the square of the field strength. The resistance of tellurium was very variable at ordinary temp., depending on the previous heat-treatment, but diminished with rise of temp. and in all cases approximated to the same value at 150° C. The increment in resistance in the magnetic field was greater at the lower temp., the curve connecting change of resistance and temp. being very similar to that for resistance and temp.

The **Hall effect** in tellurium is abnormally large (sixty times greater than in bismuth), so that if there is any close connection between the Hall effect and the change of resistance in a magnetic field one would expect the curve for the latter phenomenon to exhibit abnormal properties. The relatively large values of dR/R in tellurium, however, are small compared with those of dR/R in bismuth. P. I. Wold, and F. W. Warburton studied the Hall effect with tellurium. P. I. Wold found the Hall effect is practically independent of the field strength—up to 15,000 c.g.s. units. There is a disymmetry with reversal of field, but since this is proportional to the square of the field it is due to the Hall electrodes not being exactly on an equipotential. At ordinary temp. the Hall constant is positive, but it diminishes rapidly with rise of temp., changes sign, and with further rise of temp. reverses to positive again. The initial value depends on the heat-treatment, but there is always the double reversal as the temp. rises. It is only at ordinary temp. that widely different values of the constant are obtained ; at higher temp. the curves for different heat treatments approach each other, and the reversal to the second positive value occurs at 245° C. This behaviour cannot be regarded as due to impurities, special precautions having been taken in preparation of the specimen, and analysis showed the amount of oxide present to be exceedingly small. The author considers it due to the existence of two crystalline forms, α and β. According to W. Haken, the α modification is stable below 354° C. and the β form above this temp. The author assumes a positive Hall constant for the β modification and a negative for the α. As the Te is cooled the β form passes into the α form, but the quantity making the transition will vary. A curve connecting thermoelectric power and temp. has a shape similar to that for Hall constant and temp. Measurements of the Hall constant for liquid tellurium were unsatisfactory. The Hall effect has not been observed with amorphous substances—excluding gases—and it seems as if a crystalline structure is necessary for the Hall effect. The Ettinghausen-effect was found to be proportional to the field strength and to increase with rise of temp. The Nernst-effect was also approximately proportional to the field, but diminished in value with increase of mean temp. of the plate. The Leduc-effect was proportional to the field strength. A diminution of about 19 per cent. in the thermal conductivity was observed in a field of 6500 c.g.s., the mean temp. of the plate being 45·3° C. G. Polvani observed a lag with respect to the magnetic field of the Hall effect.

Observations on the electrolysis of dil. soln. of potassium hydroxide with tellurium electrodes were made by J. W. Ritter,[11] H. Davy, H. G. Magnus, J. C. Poggendorff, C. Himly, and G. Bredig and F. Haber—at the platinum anode, there is an evolution of oxygen, but no hydrogen is given off at the cathode. The tellurium passes into soln. as violet potassium telluride, and then is precipitated by the anodic oxygen. The observations of E. Müller, and R. Lucas are indicated above in connection with colloidal tellurium. E. Müller and R. Nowakowsky added that in 0·1N-KOH, selenium dissolves at the cathode with the valency 0·67 to 0·75, sulphur with the valency 0·57 to 0·89, and tellurium dissolves with valency about 0·9. The potentials at which soln. begins (measured against the 0·1N calomel electrode) are sulphur 0·53 volt, selenium 0·804 volt, tellurium 0·07 volt. M. le Blanc observed that tellurium as cathode readily dissolves in alkaline soln., but the dust observed by E. Müller, and R. Lucas is not obtained with very conc. soln. of potassium hydroxide. M. le Blanc found that tellurium in N-KOH dissolves both as anode and cathode. At the cathode it yields a red soln. of polytelluride. At the anode it dissolves with a valency of nearly four, in the form of $Te^{\cdot\cdot\cdot\cdot}$-ions the greater part of which react with hydroxyl ions, forming TeO_3''-ions. Tellurium is insoluble in a normal soln. of potassium hydroxide from which oxygen is excluded. In a 10N-soln., however, it dissolves at 100° to a red soln., from which it separates again on cooling or dilution. This points to the simultaneous presence of positive and negative tellurium ions. A red soln. prepared by cathodic soln. of tellurium, and containing only negative ions, is permanent. No tellurium dissolves when an alternating current is passed between tellurium electrodes in N-potassium hydroxide soln., but in $10N$-soln. dissolution takes place, the quantity dissolved increasing as the number of alternations per minute decreases. Red soln. are formed from which tellurium soon begins to separate. The observations are most simply explained by supposing that tellurium dissolves at the cathode in the form of Te''-ions and at the anode as $\text{Te}^{\cdot\cdot\cdot}$-ions. Equilibrium exists in soln. between these ions and free tellurium, $3\text{Te} \rightleftharpoons 2\text{Te}'' + \text{Te}^{\cdot\cdot\cdot\cdot}$. In very conc. alkaline soln., the equilibrium requires the presence of measurable quantities of the substances on the right-hand side of the equation, but in dil. soln. it is displaced almost entirely towards the left-hand side of the equation. According to E. Müller, the cathodic decomposition potential of tellurous acid in $2N$-sulphuric acid is —0·08 volt. No deposition potential could be obtained for tellurium from a $2N$-sulphuric acid soln. of telluric acid, from which it follows that tellurium cannot be deposited from telluric acid. According to L. Schucht, with dil. soln. of tellurous acid, tellurium is deposited loosely on the anode; and with a conc. soln. the separated tellurium floats in the liquid. E. Müller also observed that when faintly alkaline soln. of sodium tellurite or tellurate are electrolyzed there is a marked reduction to tellurium which is not hindered by the presence of chromates. According to J. Lukas and A. Jilek, a bright, adherent deposit of tellurium with a silvery lustre can be obtained by dissolving say 3 grms. of a tellurium compound in 3 c.c. of hot, conc. sulphuric acid. The cold soln. is diluted with water and 0·5 grm. of tartaric acid added, followed by ammonia until neutral to methyl-red; the soln. is acidified with 3 grms. of malonic acid, cooled to 18°, treated with 10 grms. of ammonium sulphate diluted to 120–150 c.c. and electrolyzed with a rotating anode in a platinum dish at 2 volts. The current, originally 0·03–0·09 amp., falls to 0·004–0·007 amp. when the tellurium is completely deposited. Without shutting off the current, the deposit is washed first with water, then with alcohol, dried at 100°, and weighed; it should possess a bright, silvery lustre and be firmly adherent to the dish. Tellurium is amphoteric, for, when used as cathode in the electrolysis of potassium hydroxide, J. Kasarnowsky found that it dissolves as a univalent element forming potassium telluride, K_2Te_2, but when used as anode in the electrolysis of hydrochloric acid, the tellurium passes into soln. as a quadrivalent metal forming tellurium tetrachloride. The normal potential of the system Te/Te_2'' in potassium hydroxide soln. is —0·818 volt; and with the system $\text{Te}/\text{Te}^{\cdot\cdot\cdot\cdot}$, 0·549 volt. The thermal value for the system: $3\text{Te} \rightleftharpoons \text{Te}^{\cdot\cdot\cdot\cdot} + 2\text{Te}$ is 136 Cals.; of $5\text{Te} \rightleftharpoons \text{Te}^{\cdot\cdot\cdot\cdot} + 2\text{Te}_2''$ is —129 Cals.; and $\text{Te} + \text{Te}'' = \text{Te}_2''$ is 3·5 Cals. Tellurium as a metal comes between copper and silver in the **electrochemical series,** and it is the "noblest" of the metalloids. The hypothetical system $\text{Te} \mid N\text{-Te}^{\cdot\cdot\cdot\cdot}, N\text{-Te}_2'' \mid \text{Te}$ should have an ionic product $[\text{Te}^{\cdot\cdot\cdot\cdot}][\text{Te}_2'']^2 = 10^{-95}$, which gives a measure of the amount of ionization into positive and negative ions. F. W. Bergstrom found that in liquid ammonia the electrochemical series is Pb, Bi, Sn, Sb, As, P, Te, Se, S, and I. W. Haken observed a discontinuity in the thermoelectric properties at 354° due, he supposed, to the existence of two allotropes.

H. Euler observed that the cell $\text{Te} \mid \text{sat. soln. } H_2TeO_4, N\text{-KCl} \mid \text{HgCl}$ gave no **potential difference,** but with other specimens of tellurium higher and lower values were obtained; and with the cell $\text{Te} \mid \text{TeCl}_2, N\text{-KCl} \mid \text{HgCl}$, 0·19 volt was observed by R. Lorenz and J. Egli. G. C. Schmidt in studying the passivity of metals found that there is so small a change of potential on polishing tellurium as to be scarcely detectable. G. Gallo obtained 127·61 for the **electro-chemical equivalent** of tellurium, and added that it generally goes into soln. as quadrivalent tellurium, but with N-HCl, or 10 per cent. potassium chloride, potassium nitrate, or sodium pyrophosphate and hydrochloric acid, it goes into soln. as sexivalent tellurium, never as bivalent tellurium. D. Reichinstein found for the electrode potential $\text{Te}^{\cdot\cdot\cdot\cdot} \rightarrow \text{Te}$, 0·558 volt; for $\text{Te} \rightarrow \text{Te}_2''$, —0·827; and the e.m.f. of the cell

$\mathrm{Te} \mid \mathrm{Te}^{\cdot\cdot\cdot\cdot}, \mathrm{Te}_2'' \mid \mathrm{Te}$ is 1·385 volt. The solubility product $[\mathrm{Te}^{\cdot\cdot\cdot\cdot}][\mathrm{Te}_2'']^2 = 6{\cdot}2 \times 10^{-97}$; and the constant $K = [\mathrm{Te}^{\cdot\cdot\cdot\cdot}][\mathrm{OH}']^6/[\mathrm{TeO}'']$ is 2×10^{-47}. R. Schumann found that the e.m.f. of the cell $\mathrm{Te}_{\mathrm{solid}}\mathrm{TeO}_{2\mathrm{solid}} \mid 0{\cdot}10$ to $0{\cdot}74N\text{-}\mathrm{HClO}_4 \mid \mathrm{H}_2$(1 atm.) is —0·5286 volt at 25°, and —0·5213 volt at 45°. The **reduction potential** for $\mathrm{Te}_{\mathrm{solid}} + 2\mathrm{H}_2\mathrm{O} = \mathrm{TeO(OH)}^{\cdot} + 3\mathrm{H}^{\cdot} + 4(-)$ is —0·5509 volt. J. Kasarnowsky gave —0·91 volt for the normal potential $\mathrm{Te}_2'' \rightarrow \mathrm{Te}_{\mathrm{metal}}$. F. Joliot measured the deposition potential of tellurium. A. C. Krueger and L. Kahlenberg, and S. J. French and L. Kahlenberg studied tellurium-gas cells where the gas is oxygen, hydrogen, helium, argon, or nitrogen.

E. T. Wherry[12] found tellurium to be a poor radio-detector. W. Ogawa, and I. Stransky discussed the rectifying action of tellurides. A. Günther-Schulze described the cathodic spluttering of tellurium.

The diamagnetism of tellurium was observed by J. C. Poggendorff,[13] F. Zantedeschi, and A. Oppenheim. J. Königsberger found the **magnetic susceptibility** to be $-2{\cdot}1 \times 10^{-6}$ vol. unit; S. Meyer, $-0{\cdot}6 \times 10^{-6}$ vol. unit at 18°; and A. von Ettinghausen, $-1{\cdot}6 \times 10^{-6}$ vol. unit. P. Curie gave $-0{\cdot}3 \times 10^{-6}$ mass unit between 20° and 305°; G. Wistrand, $-1{\cdot}70 \times 10^{-6}$ mass unit; P. Curie, $-0{\cdot}303 \times 10^{-3}$ mass unit; J. C. McLennan and E. Cohen, $0{\cdot}308 \times 10^{-6}$ mass unit; K. Honda, $-0{\cdot}32 \times 10^{-6}$ mass unit between 18° and 440°; and for the molten element above 440°, $-0{\cdot}04 \times 10^{-6}$ mass unit. A. Dauvillier discussed the diamagnetism and at. structure of tellurium. P. Pascal gave -378×10^{-7} for the **atomic susceptibility**; and S. S. Bhatnagar and C. L. Dhawan, $-40{\cdot}5 \times 10^{-6}$.

REFERENCES.

[1] N. W. Fischer, *Pogg. Ann.*, **12**. 502, 1828; G. Rose, *Sitzber. Akad. Berlin*, 72, 1849; *Pogg. Ann.*, **77**. 146, 1849; **83**. 126, 1851; J. J. Berzelius, *ib.*, **8**. 411, 1826; **28**. 392, 1833; **32**. 1, 577, 1834; *Schweigger's Journ.*, **6**. 311, 1812; **34**. 78, 1823; P. P. Ewald and C. Hausmann, *Zeit. Kryst.*, **65**. Suppl., 28, 1927; L. Tokody, *Centr. Min.*, 114, 1929; L. P. Sieg, *Phys. Rev.*, (2), **25**. 116, 1925; H. Staudinger and W. Kreis, *Helvetica Chim. Acta*, **8**. 71, 1925; W. Phillips, *Elementary Introduction to Mineralogy*, London, 327, 1823; A. W. Wright, *Amer. Journ. Science*, (3), **13**. 49, 1877; (3), **14**. 169, 1877; H. G. Grimm and H. Wolff, *Zeit. phys. Chem.*, **119**. 254, 1926; H. G. Grimm, *ib.*, **122**. 177, 1926; A. Breithaupt, *Vollständige Charakteristik des Mineralsystems*, Dresden, 261, 1832; *Schweigger's Journ.*, **52**. 169, 1828; F. Fouqué and A. Michel-Lévy, *Synthèse des minéraux et des roches*, Paris, 393, 1882; V. R. von Zepharovich, *Mineralogisches Lexikon für des Kaiserthum Oesterreich*, Wien, **3**. 246, 1893; A. des Cloizeaux, *Manuel de minéralogie*, Paris, **2**. 304, 1893; M. H. Klaproth, *Mem. Akad. Berlin*, **50**. 17, 1798; *Beiträge zur chemischen Kenntniss der Mineralkörper*, Berlin, **3**. 1, 1802; London, **2**. 1, 1804; *Crell's Ann.*, **1**. 91, 1798; *Gilbert's Ann.*, **12**. 246, 1802; A. Ferrari, *Nuovo Cimento*, (7), **4**. 1, 1927; F. J. Müller von Reichenstein, *Phys. Arb. Freunde Wien*, **1**. 1, 1782; **3**. 48, 1785; J. Löwe, *Journ. prakt. Chem.*, (1), **60**. 163, 1853; *Sitzber. Akad. Wien*, **10**. 727, 1853; W. Spring, *Bull. Acad. Belg.*, (3), **2**. 88, 1881; L. S. Ramsdell, *Amer. Min.*, **10**. 281, 1925; D. Klein and L. Morel, *Ann. Chim. Phys.*, (6), **5**. 61, 1885; E. Priwoznik, *Vorkommen von Tellur und Gewinnung aus seinen Erzen*, Wien, 1893; *Oesterr. Zeit. Berg. Hütt.*, **45**. 219, 1885; W. F. de Jong and H. W. V. Williams, *Physica*, **7**. 74, 1927; R. W. E. MacIvor, *Chem. News*, **82**. 272, 1900; J. C. L. Schroeder van der Kolk, *Centr. Min.*, 76, 1901; V. Lenher and J. L. R. Morgan, *Journ. Amer. Chem. Soc.*, **22**. 28, 1900; H. Fay and C. B. Gillson, *Amer. Chem. Journ.*, **27**. 81, 1902; J. F. Norris and R. Mommers, *ib.*, **23**. 486, 1900; J. F. Norris and W. A. Kingman, *ib.*, **26**. 318, 1901; A. Wigand, *Ann. Physik*, (6), **22**. 64, 1907; W. L. Bragg, *Phil. Mag.*, (6), **40**. 169, 1920; E. Matthey, *Proc. Roy. Soc.*, **68**. 161, 1901; Y. Kimata, *Mem. Coll. Science Kyoto*, **1**. 119, 1915; I. I. Saslavsky, *Isvestia Ivanovo-Vosnessenskovo Politech. Inst.*, **1**. 61, 1919; A. J. Bradley, *Phil. Mag.*, (6), **48**. 477, 1924; M. K. Slattery, *Phys. Rev.*, (2), **21**. 378, 1923; (2), **25**. 333, 1925; M. L. Huggins, *ib.*, (2), **21**. 208, 1923; (2), **28**. 1086, 1926; L. P. Sieg, *ib.*, (2), **25**. 116, 1925; F. Krafft and O. Steiner, *Ber.*, **34**. 560, 1901; O. Steiner, *Beiträge zur Kenntniss der Schwelfel-Selen-Tellur-Gruppe*, Heidelberg, 1900; R. Auerbach, *Zeit. phys. Chem.*, **121**. 337, 1920; H. L. Wheeler, *Amer. Journ. Science*, (3), **45**. 267, 1893; *Zeit. anorg. Chem.*, **3**. 428, 1893; G. Wassermann, *Ueber Untersuchungen an Tellurkristallen*, Berlin, 1928; E. Schmid and G. Wassermann, *Zeit. Physik*, **46**. 653, 1928; R. F. Mehl and B. J. Mair, *Journ. Amer. Chem. Soc.*, **49**. 1892, 1927; P. Saldau, *Ann. St. Petersburg Inst. Mines*, **4**. 228, 1913; E. Moles, *Anal. Fis. Quim.*, **13**. 134, 1915; A. Jouniaux, *Bull. Soc. Chim.*, (4), **35**. 1607, 1924; H. von Wartenberg, *Zeit. anorg. Chem.*, **56**. 320, 1907; P. W. Bridgman, *Proc. Amer. Acad.*, **60**. 366, 1925; *Phys. Rev.*, (2), **9**. 138, 1917; *Proc. Roy. Acad.*, **10**. 411, 1924; D. Beljankin, *Journ. Russ. Phys. Chem. Soc.*, **33**. 670, 1901; D. Gernez, *Compt. Rend.*, **74**. 803, 1190, 1870; W. Haken, *Ber. deut. phys. Ges.*,

12. 229, 1910 ; G. Tammann, *Kristallisieren und Schmelzen*, Leipzig, 58, 1903 ; C. Haushofer, *Mikroskopische Reaktionen*, Braunschweig, 124, 1885 ; C. F. Rammelsberg, *Sitzber. Akad. Berlin*, 380, 1879 ; *Handbuch der Mineralchemie*, Leipzig, **1.** 92, 1875 ; *Handbuch der krystallographisch-physikalischen Chemie*, Leipzig, **1.** 115, 1881 ; P. Groth, *Chemische Krystallographie*, Leipzig, **1.** 35, 1906 ; R. Auerbach, *Zeit. phys. Chem.*, **121.** 337, 1926 ; *Koll. Zeit.*, **38.** 343, 1926 ; J. W. Retgers, *Zeit. phys. Chem.*, **8.** 70, 1891 ; **9.** 399, 1892 ; **10.** 533, 1892 ; **12.** 593, 1893 ; **14.** 17, 1894 ; **16.** 611, 656, 1895 ; *Zeit. anorg. Chem.*, **3.** 349, 1893 ; **12.** 103, 1894 ; W. Muthmann, *Ber.*, **26.** 1008, 1893 ; *Zeit. anorg. Chem.*, **10.** 218, 1895 ; G. W. A. Kahlbaum, *ib.*, **29.** 288, 1902 ; G. W. A. Kahlbaum, K. Roth and P. Siedler, *ib.*, **29.** 177, 1902 ; C. del Fresno, *ib.*, **153.** 28, 1926 ; F. A. Genth, *Proc. Amer. Phil. Soc.*, **17.** 113, 1877 ; R. Schelle, *Proc. Internat. Congress Appl. Chem.*, **7.** iii, 80, 1909 ; G. Pellini and G. Vio, *Atti Accad. Lincei*, (5), **15.** ii, 46, 1906 ; G. Pellini, *ib.*, (5), **15.** i, 629, 711, 1926 ; (5), **18.** i, 701, 1909 ; (5), **18.** ii, 19, 1909 ; (5), **21.** i, 218, 1912 ; G. Magnus, *Dissertatio de tellurio*, Beroleusis, 1827 ; *Pogg. Ann.*, **17.** 521, 1829 ; G. W. Zenger, *Sitzber. Akad. Wien*, **44.** 308, 1861 ; J. Margottet, *Compt. Rend.*, **85.** 1142, 1877 ; *Recherches sur les sulfures, les séléniures, et les telluriures métalliques*, Paris, 1879 ; *Ann. École Norm.*, **8.** 247, 1879 ; G. vom Rath, *Verh. Naturh. Ver. Bonn.*, 296, 1884 ; J. Loczka, *Zeit. Kryst.*, **20.** 317, 1892 ; S. von Olshausen, *ib.*, **61.** 463, 1925 ; G. Rolland, *Ann. Mines*, (6), **13.** 159, 1878 ; H. von Foullon, *Verh. geol. Reichsanst. Wien*, 269, 1884 ; E. Billows, *Rev. Min. Crist. Ital.*, **38.** 91, 1909 ; A. Damiens, *Ann. Chim. Phys.*, (9), **18.** 282, 1922 ; *Compt. Rend.*, **174.** 1344, 1548, 1922 ; V. M. Goldschmidt, *Zeit. Elektrochem.*, **34.** 453, 1928 ; E. T. Wherry, *Amer. Min.*, **14.** 54, 1930 ; F. H. Burstall and S. Sugden, *Journ. Chem. Soc.*, 229, 1930 ; W. Hume-Rothery, *Phil. Mag.*, (7), **9.** 65, 1930 ; (7), **10.** 217, 1930 ; J. C. Slater, *Phys. Rev.*, (2), **36.** 57, 1930.

[2] E. Cohen and J. F. Kröner, *Zeit. phys. Chem.*, **82.** 587, 1913 ; A. Damiens, *Compt. Rend.*, **174.** 1344, 1548, 1922 ; *Ann. Chim. Phys.*, (9), **18.** 282, 1922 ; *Bull. Soc. Chim.*, (4), **35.** 87, 1924 ; C. del Fresno, *Zeit. anorg. Chem.*, **152.** 28, 1926 ; W. Haken, *Ber. deut. phys. Ges.*, **12.** 229, 1910 ; I. I. Saslavsky, *Isvestia Ivanovo-Vosnessenskovo Politech. Inst.*, **1.** 61, 1919 ; L. S. Ramsdell, *Amer. Min.*, **10.** 281, 1925 ; H. G. Grimm, *Zeit. phys. Chem.*, **122.** 177, 1926 ; H. Staudinger and W. Kreis, *Helvetica Chim. Acta.*, **8.** 71, 1925.

[3] W. Spring, *Bull. Acad. Belg.*, (3), **2.** 88, 1881 ; J. R. Rydberg, *Zeit. phys. Chem.*, **33.** 553, 1900 ; H. Fizeau, *Compt. Rend.*, **68.** 1125, 1869 ; E. Jannetaz, *ib.*, **114.** 1352, 1892 ; *Bull. Soc. Min.*, **15.** 137, 1892 ; E. Schmid and G. Wassermann, *Zeit. Physik*, **46.** 653, 1928 ; J. Dewar, *Proc. Roy. Soc.*, **89.** A, 158, 1913 ; W. A. Tilden, *Phil. Trans.*, **203.** A, 139, 1904 ; A. Wigand, *Ann. Physik*, (4), **22.** 64, 1907 ; G. W. A. Kahlbaum, K. Roth and P. Siedler, *Zeit. anorg. Chem.*, **29.** 177, 1902 ; M. Toepler, *Wied. Ann.*, **53.** 363, 1894 ; H. V. Regnault, *Ann. Chim. Phys.*, (3), **46.** 257, 1856 ; M. Berthelot and C. Fabre, *ib.*, (6), **14.** 101, 1887 ; H. Kopp, *Phil. Trans.*, **155.** 71, 1865 ; *Liebig's Ann. Suppl.*, **3.** 289, 1865 ; P. W. Bridgman, *Proc. Amer. Acad.*, **60.** 366, 1925 ; *Phys. Rev.*, (2), **9.** 135, 1917 ; *Journ. Washington Acad.*, **17.** 529, 1927 ; *Proc. Nat. Acad.*, **10.** 411, 1924 ; R. F. Mehl and B. J. Mair, *Journ. Amer. Chem. Soc.*, **49.** 1892, 1927 ; P. Saldau, *Ann. St. Petersburg Inst. Mines*, **4.** 228, 1913.

[4] T. Carnelley and W. C. Williams, *Journ. Chem. Soc.*, **37.** 125, 1880 ; R. Pictet, *Compt. Rend.*, **88.** 1317, 1879 ; H. Pélabon, *Ann. Chim. Phys.*, (8), **17.** 526, 1909 ; *Compt. Rend.*, **145.** 118, 1907 ; **146.** 1397, 1908 ; **148.** 1176, 1909 ; H. St. C. Deville and L. Troost, *ib.*, **56.** 81, 1863 ; **91.** 83, 1880 ; M. Berthelot and C. Fabre, *ib.*, **105.** 92, 1887 ; *Bull. Soc. Chim.*, (2), **48.** 692, 1887 ; M. H. Klaproth, *Mem. Akad. Berlin*, **50.** 17, 1798 ; *Beiträge zur chemischen Kenntniss der Mineralkörpen*, Berlin, **3.** 1, 1902 ; London, **2.** 1, 1904 ; *Crell's Ann.*, **1.** 91, 1798 ; *Gilbert's Ann.*, **12.** 246, 1902 ; H. Fay and C. B. Gilson, *Trans. Amer. Inst. Min. Eng.*, **31.** 527, 1901 ; *Amer. Chem. Journ.*, **27.** 81, 1902 ; H. Fay and H. E. Ashley, *ib.*, **27.** 95, 1902 ; E. Matthey, *Proc. Roy. Soc.*, **68.** 161, 1901 ; J. J. Berzelius, *Schweigger's Journ.*, **6.** 311, 1812 ; **34.** 78, 1823 ; *Pogg. Ann.*, **8.** 411, 1826 ; **28.** 392, 1833 ; **32.** 1, 577, 1834 ; F. Exner, *Sitzber. Akad. Wien*, **73.** 285, 1876 ; *Pogg. Ann.*, **158.** 646, 1876 ; F. Wöhler, *ib.*, **11.** 161, 1827 ; G. N. Lewis and G. E. Gilson, *Journ. Amer. Chem. Soc.*, **39.** 2554, 1917 ; G. N. Lewis and W. M. Latimer, *ib.*, **44.** 1008, 1923 ; G. N. Lewis and M. Ramsdell. *ib.*, **36.** 2468, 1914 ; S. Umino, *Kinzoku no Kenku*, **3.** 498, 1926 ; E. Adinolefi, *Atti Accad. Lincei*, (6), **8.** 381, 1928 ; B. Bruzs, *Journ. Phys. Chem.*, **31.** 581, 1927 ; K. Mönkemeyer, *Zeit. anorg. Chem.*, **45.** 418, 1905 ; W. Herz, *ib.*, **170.** 237, 1928 ; H. Biltz, *Sitzber. Akad. Berlin*, 63, 1896 ; W. Biltz and W. Meckenburg, *Zeit. anorg. Chem.*, **64.** 226, 1909 ; W. Herz, *ib.*, **175.** 245, 1928 ; **177.** 116, 1928 ; **179.** 277, 1929 ; **180.** 284, 1929 ; L. Staudenmaier, *ib.*, **10.** 197, 1895 ; M. Chikashige, *ib.*, **54.** 50, 1907 ; M. Kobayashi, *ib.*, **69.** 1, 1910 ; W. Guertler and M. Pirani, *Zeit. Metallkunde*, **11.** 1, 1911 ; F. Krafft and L. Merz, *Ber.*, **37.** 4344, 1903 ; F. Krafft, *ib.*, **36.** 1690, 1903 ; L. Merz, *Ueber das Verhalten der Elemente und Verbindungen der Schwefelgruppe im Vakuum*, Heidelburg, 1905 ; H. Carlsohn, *Ber.*, **59.** B, 1916, 1926 ; A. Schuller, *Wied. Ann.*, **18.** 320, 1883 ; *Ber. Ungarn. Naturwiss.*, **1.** 64, 1884 ; J. Joly, *Phil. Mag.*, (6), **27.** 1, 1914 ; A. Oppenheim, *Journ. prakt. Chem.*, (1), **71.** 267, 1857 ; *Beobachtungen über das Tellur und einige reiner Verbindungen*, Göttingen, 1857 ; E. Kordes, *Zeit. anorg. Chem.*, **160.** 67, 1927 ; A. Damiens, *Ann. Chim. Phys.*, (9), **19.** 44, 1922 ; *Compt. Rend.*, **174.** 1344, 1548, 1902 ; J. J. Doolan and J. R. Partington, *Trans. Faraday Soc.*, **20.** 342, 1924 ; W. R. Mott, *Trans. Amer. Electrochem. Soc.*, **34.** 555, 1918 ; I. Maydel, *Zeit. anorg. Chem.*, **186.** 289, 1930 ; V. Kondratéeff, *Zeit. phys. Chem.*, **7.** B, 70, 1930 ; A. Simek and B. Stehlik, *Coll. Czech. Chem. Comm.*, **2.** 304, 1930 ; J. J. van Laar, *Zeit. Physik*, **62.** 77, 1930 ; J. Franck, *Zeit. Elektrochem.*, **36.** 581, 1930.

[5] K. Spangenberg, *Naturwiss.*, **15.** 266, 1927 ; C. Cuthbertson and E. P. Metcalfe, *Phil. Trans.*,

207. A, 135, 1908 ; G. Pellini and A. Menin, *Gazz. Chim. Ital.*, **30**. ii, 465, 1900 ; J. E. Calthrop, *Phil. Mag.*, (6), **47**. 772, 1924 ; W. W. Coblentz, *Journ. Franklin Inst.*, **170**. 186, 1910 ; *Bull. Soc. Standards*, **2**. 457, 1906 ; **7**. 197, 1911 ; L. P. Sieg, *Phys. Rev.*, (2), **21**. 211, 1923 ; L. P. Sieg and G. D. van Dyke, *ib.*, (2), **21**. 206, 1923 ; G. D. van Dyke, *Journ. Amer. Opt. Soc.*, **6**. 917, 1922 ; R. F. Miller, *ib.*, **10**. 621, 1925 ; *Phys. Rev.*, (2), **23**. 306, 1926 ; M. A. Schirmann, *Phys. Zeit.*, **23**. 441, 1922 ; A. H. Pfund, *Journ. Amer. Opt. Soc.*, **12**. 467, 1926 ; E. O. Hulburt, *Astrophys. Journ.*, **42**. 222, 1915.

[6] R. T. Simmler, *Pogg. Ann.*, **115**. 242, 425, 1862 ; A. Mischerlich, *ib.*, **121**. 459, 1864 ; J. C. McLennan, I. Walerstein and H. G. Smith, *Phil. Mag.*, (7), **3**. 390, 1927 ; W. A. Miller, *Phil. Trans.*, **152**. 861, 1862 ; T. R. Robinson, *ib.*, **152**. 929, 1862 ; W. Huggins, *ib.*, **154**. 139, 1864 ; R. J. Lang, *ib.*, **224**. A, 371, 1924 ; W. N. Hartley and W. F. Adeney, *ib.*, **175**. 63, 1884 ; W. N. Hartley, *ib.*, **175**. 325, 1884 ; **185**. A, 161, 1029, 1894 ; *Trans. Roy. Soc. Dublin*, (2), **1**. 231, 1882 ; *Journ. Chem. Soc.*, **41**. 84, 1882 ; **71**. 533, 1891 ; *Proc. Roy. Soc.*, **49**. 448, 1891 ; **54**. 5, 1893 ; R. Thalén, *Om Spectralanalyse*, Upsala, 1866 ; *Nova Acta Upsala*, (3), **6**. 9, 1868 ; G. Werther, *Journ. prakt. Chem.*, (1), **88**. 180, 1863 ; J. C. McLennan and R. F. B. Cooley, *Trans. Roy. Soc. Canada*, (3), **20**. 349, 1926 ; E. J. Allin, *ib.*, (3), **21**. 231, 1927 ; J. C. McLennan, A. B. McLay and J. H. McLeord, *Phil. Mag.*, (7), **4**. 486, 1927 ; J. C. McLennan and A. C. Lewis, *Proc. Roy. Soc.*, **98**. A, 109, 1920 ; J. J. Dobbie and A. J. Fox, *ib.*, **98**. A, 109, 1920 ; J. J. Dobbie and A. J. Fox, *ib.*, **98**. A, 147, 1920 ; A. Ditte, *Compt. Rend.*, **73**. 622, 1871 ; D. Gernez, *ib.*, **74**. 803, 1190, 1872 ; G. Salet, *ib.*, **73**. 742, 1871 ; *Ann. Chim. Phys.*, (4), **28**. 5, 1873 ; *Traité élémentaire de spectroscopie*, Paris, 1888 ; A. de Gramont, *Analyse spectrale direct des minéraux*, Paris, 1897 ; *Compt. Rend.*, **127**. 866, 1898 ; **134**. 1048, 1902 ; **146**. 1260, 1907 ; L. and E. Block, *Ann. Physique*, (10), **13**. 235, 1930 ; *Compt. Rend.*, **187**. 562, 1928 ; E. Demarçay, *ib.*, **99**. 1022, 1069, 1884 ; *Spectres electriques*, Paris, 1895 ; R. Capron, *Photographed Spectra*, London, 1877 ; A. W. Wright, *Amer. Journ. Science*, (3), **13**. 49, 1877 ; (3), **14**. 169, 1877 ; H. S. Uhler and R. A. Patterson, *ib.*, (4), **36**. 135, 1913 ; C. L. Ciamician, *Sitzber. Akad. Wien*, **82**. 425, 1880 ; J. M. Eder and E. Valenta, *ib.*, **118**. 1077, 1909 ; *Atlas typischen Spectren*, Wien, 1911 ; R. Exner and E. Haschek, *Die Spectren der Elemente bei normalen Druck*, Leipzig, 1911 ; *Wellenlängentabellen für spectralanalytische Untersuchungen auf Grund der ultravioletten Bogenspectren der Elemente*, Leipzig, 1904 ; *Wellenlängtabellen für spectralanalytische Untersuchungen auf Grund der ultravioletten Funkenspectren der Elemente*, Leipzig, 1902 ; *Sitzber. Akad. Wien*, **106**. 337, 1897 ; A. Hagenbach and H. Konen, *Atlas der Emissionsspectren der meisten Elemente*, Jena, 1905 ; W. Friederichs, *Ueber Absorptionsspectra von Dämpfen*, Bonn, 1905 ; A. Michaelis, *Ber.*, **20**. 2488, 1887 ; V. Schumann, *Photogr. Rend.*, **41**. 71, 1890 ; P. Köthner, *Liebig's Ann.*, **319**. 1, 1901 ; R. Mecke, *Zeit. Physik*, **42**. 390, 1927 ; B. Rosen, *ib.*, **43**. 69, 1927 ; J. Trowbridge and W. C. Sabine, *Phil. Mag.*, (5), **26**. 316, 1888 ; C. Runge and F. Paschen, *Wied. Ann.*, **61**. 641, 1897 ; *Astrophys. Journ.*, **8**. 70, 1898 ; P. Lewis, *ib.*, **16**. 31, 1902 ; *Phys. Zeit.*, **3**. 498, 1902 ; J. Stark and R. Küch, *ib.*, **6**. 438, 1905 ; H. Nagaoka, D. Nukiyama, and T. Futagami, *Proc. Acad. Japan*, **3**. 392, 398, 403, 409, 415, 1927 ; F. K. Bell, *Ber.*, **60**. B, 1749, 1927 ; P. Lacroute, *Journ. Phys. Rad.*, (6), **9**. 180, 1928 ; A. M. Vieweg, C. W. Gartlein and R. C. Gibbs, *Phys. Rev.*, (2), **33**. 287, 1929 ; R. J. Lang, *Proc. Nat. Acad.*, **13**. 341, 1927 ; P. G. Nutting, *Bull. Bur. Standards*, **1**. 83, 399, 1904 ; *Astrophys. Journ.*, **22**. 131, 1905 ; M. Kimura, *Japan. Journ. Phys.*, **4**. 81, 1927 ; E. Gehrcke and O. von Baeyer, *Ann. Physik*, (4), **20**. 269, 1906 ; E. Goldstein, *ib.*, (4), **27**. 773, 1908 ; W. L. Dudley and E. V. Jones, *Journ. Amer. Chem. Soc.*, **34**. 995, 1912 ; J. R. Pogorzelska, *Compt. Rend. Soc. Polonaise Phys.*, **7**. 51, 1926 ; E. Paterno and A. Mazzucchelli, *Atti Accad. Lincei*, (5), **17**. 428, 1908 ; A. Grünwald, *Monatsh.*, **9**. 829, 1889 ; R. V. Zumstein, *Phys. Rev.*, (2), **27**. 562, 1926 ; R. C. Gibbs and A. M. Vieweg, *ib.*, (2), **34**. 400, 1929 ; E. Rütten, *Zeit. Physik*, **60**. 1, 1930 ; H. Schüler and H. Brück, *ib.*, **58**. 735, 1929 ; A. Przeborsky, *ib.*, **63**. 280, 1930 ; C. H. Cartwright, *Phys. Rev.*, (2), **35**. 415, 1930 ; E. V. Condon and G. H. Shortley, *ib.*, (2), **35**. 1342, 1930.

[7] W. Steubing, *Phys. Zeit.*, **14**. 887, 1913 ; D. Diestelmeier, *Ueber die Fluoreszenz von Schwefel- Selen-, und Tellurdampf.*, Münster, 1914 ; *Zeit. wiss. Photochem.*, **13**. 18, 1915 ; W. Kessel, *Compt. Rend.*, **189**. 94, 1929 ; H. R. Pogorzelska, *Bull. Acad. Polonaise*, 243, 1926 ; J. C. McLennan, I. Waterstein and H. G. Smith, *Phil. Mag.*, (7), **3**. 390, 1927 ; B. Rosen, *Zeit. Physik*, **43**. 69, 1927 ; W. Steubing, *Verh. deut. phys. Ges.*, **15**. 1181, 1913 ; A. Smekal, *Zeit. Elektrochem.*, **36**. 618, 1930.

[8] F. C. Blake and W. Duane, *Phys. Rev.*, (2), **10**. 697, 1917 ; J. M. Cork and B. R. Stephenson, *ib.*, (2), **27**. 530, 1926 ; B. B. Ray, *Phil. Mag.*, (6), **48**. 707, 1924 ; K. Chamberlain and G. A. Lindsay, *Phys. Rev.*, (2), **30**. 369, 1927 ; M. Siegbahn, *Jahrb. Rad. Elektron.*, **13**. 296, 1916 ; *Ber. deut. phys. Ges.*, **18**. 39, 1916 ; M. Siegbahn and E. Jönsson, *Phys. Zeit.*, **20**. 251, 1919 ; W. Herz, *Zeit. anorg. Chem.*, **163**. 220, 1927 ; **170**. 237, 1928 ; **175**. 245, 1928 ; **177**. 116, 1928 ; D. Coster, *Phil. Mag.*, (6), **43**. 1070, 1923 ; *Zeit. Physik*, **25**. 83, 1924 ; *Compt. Rend.*, **174**. 378, 1922 ; M. Lindsay, *ib.*, **175**. 150, 1922 ; K. Chamberlain and G. A. Lindsay, *Phys. Rev.*, (2), **30**. 369, 1927 ; D. Coster and F. P. Müller, *Zeit. Physik*, **38**. 264, 1926 ; E. Hjalmar, *ib.*, **3**. 262, 1920 ; B. Walter, *ib.*, **30**. 357, 1924 ; S. Björck, *ib.*, **53**. 228, 1929 ; A. Leide, *ib.*, **39**. 686, 1926 ; *Compt. Rend.*, **180**. 1203, 1925 ; H. Hirata, *Proc. Roy. Soc.*, **105**. A, 40, 1922 ; B. B. Ray, *Phil. Mag.*, (6), **48**. 707, 1924 ; Y. Nishina, *ib.*, (6), **49**. 522, 1925.

[9] N. Piltschikoff, *Phys. Zeit.*, **7**. 69, 1906 ; R. S. Bartlett, *Phys. Rev.*, (2), **96**. 247, 1925 ; B. Rosen, *Naturwiss.*, **14**. 978, 1926 ; H. Müller, *Sitzber. Akad. Wien*, **135**. 563, 1926 ; E. Rupp, *Zeit. Physik*, **58**. 145, 1929 ; G. Piccardi, *Atti Accad. Lincei*, (6), **6**. 305, 1927 ; T. Pavolini,

Giorn. Chim. Ind. Appl., **12**. 72, 1930 ; J. Vrede, *Phys. Zeit.*, **31**. 323, 1930 ; E. Rabonowitsch and E. Thilo, *Zeit. phys. Chem.*, **6**. B, 284, 1929.

[10] C. W. Heaps, *Phil. Mag.*, (6), **24**. 814, 1912 ; A. Matthiessen, *ib.*, (4), **16**. 219, 1858 ; *Phil. Trans.*, **148**. 383, 1858 ; *Pogg. Ann.*, **103**. 428, 1858 ; A. Matthiessen and M. von Bose, *ib.*, **115**. 352, 1862 ; *Phil. Trans.*, **152**. 1, 1862 ; *Proc. Roy. Soc.*, **11**. 516, 1862 ; P. E. Shaw and C. S. Jex, *ib.*, **118**. A, 97, 1928 ; P. Kapitza, *ib.*, **123**. A, 292, 342, 1929 ; E. Matthey, *ib.*, **68**. 161, 1901 ; W. G. Adams, *ib.*, **24**. 163, 1876 ; *Phil. Mag.*, (5), **1**. 322, 1876 ; *Pogg. Ann.*, **159**. 529, 1876 ; F. Exner, *ib.*, **158**. 646, 1876 ; *Wied. Ann.*, **2**. 100, 1877 ; *Sitzber. Akad. Wien*, **73**. 285, 1876 ; **75**. 378, 1877 ; A. von Ettinghausen, *ib.*, **95**. 714, 1888 ; C. A. Kraus and E. W. Johnson, *Journ. Phys. Chem.*, **32**. 1281, 1928 ; M. A. Levitsky and M. A. Lukomsky, *Phys. Zeit.*, **30**. 203, 1929 ; H. K. Onnes and W. Tayn, *Comm. Phys. Lab. Leiden*, Suppl. 58, 1926 ; B. Beckman, *ib.*, 40, 1915 ; H. K. Onnes and B. Beckman, *ib.*, 132, d, 1912 ; *Proc. Acad. Amsterdam*, **15**. 997, 1912 ; *Versl. Akad. Amsterdam*, **21**. 1044, 1912 ; B. Beckman, *Ueber den Einfluss der Druckes auf die elektrisch Leitfähigkeit bei Pyrit, Eisenglanz, und Metallegierungen*, Upsala, 1911 ; *Arkiv. Math. Astr. Fys.*, **7**. 42, 1902 ; *Phys. Zeit.*, **16**. 59, 1915 ; *Ann. Physik*, (4), **46**. 477, 931, 1915 ; J. M. Rivière, *Sur la résistance électrique de quelques mélanges de tellure et d'argent, et ses variations avec la temperature*, Paris, 1911 ; V. Lenher and J. L. R. Morgan, *Journ. Amer. Chem. Soc.*, **22**. 28, 1900 ; R. Schuhmann, *ib.*, **47**. 356, 1925 ; W. Haken, *Ber. deut. phys. Ges.*, **12**. 229, 1910 ; *Ann. Physik*, (4), **32**. 291, 1910 ; B. Lange and W. Heller, *Phys. Zeit.*, **30**. 419, 1929 ; A. Günther-Schulze, *Zeit. Elektrochem.*, **33**. 360, 1927 ; A. Schulze, *Zeit. Metallkunde*, **15**. 155, 1923 ; **16**. 48, 1924 ; F. Beijerinck, *Neues Jahrb. Min. B.B.*, **11**. 423, 1897 ; E. Cohen and J. F. Kröner, *Zeit. phys. Chem.*, **82**. 597, 1913 ; A. de la Rive, *Mém. Sciences Genève*, **6**. 149, 1833 ; *Phil. Mag.*, (3), **9**. 274, 1837 ; H. Perlitz, *ib.*, (7), **2**. 1148, 1926 ; W. Ogawa, *Journ. Japan. Soc. Chem. Ind.*, **31**. 476, 1928 ; L. Amaduzzi and M. Padoa, *Nuovo Cimento*, (6), **3**. i, 66, 1912 ; G. Polvani, *ib.*, (7), **3**. 184, 1926 ; A. Guntz and W. Broniewsky, *Compt. Rend.*, **147**. 1474, 1908 ; J. Kasarnowsky, *Zeit. anorg. Chem.*, **128**. 17, 33, 1923 ; **130**. 140, 1923 ; P. W. Bridgman, *Proc. Nat. Acad.*, **10**. 411, 1924 ; *Proc. Amer. Acad.*, **52**. 623, 1917 ; **61**. 101, 1926 ; R. S. Bartlett, *Phys. Rev.*, (2), **26**. 247, 1925 ; P. I. Wold, *ib.*, (2), **7**. 169, 1916 ; K. F. Herzfeld, *ib.*, (2), **29**. 701, 1927 ; F. W. Warburton, *ib.*, (2), **29**. 905, 1927 ; (2), **30**. 673, 1927 ; T. W. Case, *ib.*, (2), **9**. 303, 1917 ; E. Teichmann, *Zeit. Physik*, **59**. 615, 1930.

[11] J. W. Ritter, *Denks. München Akad.*, 210, 1808 ; *Gehlen's Journ.*, **6**. 568, 1808 ; *Gilbert's Journ.*, **29**. 148, 1808 ; H. G. Magnus, *Dissertatio de tellurio*, Berolensis, 1827 ; *Pogg. Ann.*, **17**. 521, 1829 ; J. C. Poggendorff, *ib.*, **75**. 349, 1848 ; T. W. Case, *Phys. Rev.*, (2), **9**. 303, 1917 ; C. Himly, *Schriften Naturwiss.*, 117, 1877 ; F. W. Bergstrom, *Journ. Amer. Chem. Soc.* **47**. 1503, 1925 ; F. Joliot, *Compt. Rend.*, **188**. 1106, 1929 ; H. Davy, *Phil. Trans.*, **100**. 16, 1910 ; L. Schucht, *Berg. Hütt. Ztg.*, **39**. 121, 1880 ; *Chem. News*, **41**. 280, 1880 ; *Zeit. anal. Chem.*, **22**. 485, 1883 ; *Chem. Ztg.*, **4**. 272, 1880 ; C. Bredig and F. Haber, *Ber.*, **31**. 2741, 1898 ; R. Schumann, *Journ. Amer. Chem. Soc.*, **47**. 356, 1925 ; E. Müller, *Ber.*, **36**. 4262, 1903 ; W. Haken, *Ber. deut. phys. Ges.*, **12**. 229, 1910 ; D. Reichinstein, *Zeit. phys. Chem.*, **97**. 257, 1921 ; G. C. Schmidt, *ib.*, **106**. 105, 1923 ; E. Müller, *ib.*, **100**. 346, 1922 ; S. J. French and L. Kahlenberg, *Metal Ind.*, **33**. 443, 543, 569, 1928 ; *Trans. Amer. Electrochem. Soc.*, **54**. 163, 1928 ; A. C. Krueger and L. Kahlenberg, *ib.*, **58**. , 1930 ; R. Lucas, *Zeit. Elektrochem.*, **11**. 521, 1905 ; E. Müller and R. Nowakowsky, *ib.*, **11**. 931, 1905 ; M. le Blanc, *ib.*, **11**. 813, 1905 ; **12**. 649, 1906 ; R. Lorentz and J. Egli, *Zeit. anorg. Chem.*, **41**. 95, 1904 ; H. Euler, *ib.*, **41**. 93, 1904 ; G. Gallo, *Atti Accad. Lincei*, (5), **14**. i, 23, 104, 1905 ; *Gazz. Chim. Ital.*, **35**. ii, 245, 1905 ; J. Kasarnowsky, *Die Stellung des Tellurs und Selens in der Volta'schen Spannungsreihe*, Zürich, 1915 ; *Zeit. anorg. Chem.*, **128**. 17, 33, 1923 ; **130**. 140, 1923 ; J. Lucas and A. Jilek, *Chem. Listy*, **20**. 396, 1926.

[12] E. T. Wherry, *Amer. Min.*, **10**. 28, 1925 ; A. Günther-Schulze, *Zeit. Physik*, **36**. 563, 1926 ; I. Stransky, *Zeit. phys. Chem.*, **113**. 131, 1924 ; W. Ogawa, *Journ. Japan. Soc. Chem. Ind.*, **31**. 486, 1928.

[13] J. C. Poggendorff, *Pogg. Ann.*, **73**. 619, 1848 ; *Ber. Berlin Acad.*, 485, 1847 ; F. Zantedeschi, *Giorn. Fis. Chim. Ital.*, 1, 1852 ; A. Oppenheim, *Journ. prakt. Chem.*, (1), **71**. 267, 1857 ; A. von Ettinghausen, *Sitzber. Akad. Wien*, **96**. 777, 1887 ; *Wied. Ann.*, **17**. 272, 1882 ; J. Königsberger, **66**. 698, 1898 ; *Ann. Physik*, (4), **6**. 506, 1901 ; K. Honda, *ib.*, (4), **32**. 1027, 1910 ; M. Owen, *ib.*, (4), **37**. 657, 1912 ; S. Meyer, *ib.*, (4), **1**. 664, 668, 1900 ; *Wied. Ann.*, **68**. 325, 1899 ; **69**. 236, 1899 ; S. S. Bhatnagar and C. L. Dhawan, *Phil. Mag.*, (7), **5**. 536, 1928 ; P. Curie, *Compt. Rend.*, **115**. 1292, 1892 ; **116**. 136, 1893 ; *Journ. Phys.*, (3), **4**. 197, 1895 ; G. Wistrand, *Magnetiska Susceptibiliteten hos Kvarts, Tellur och några Holmiumföreningar*, Upsala, 1926 ; A. Dauvillier, *Compt. Rend.*, **176**. 1802, 1923 ; P. Pascal, *Rev. Gen. Science*, **34**. 388, 1923 ; J. C. McLennan and E. Cohen, *Trans. Roy. Soc. Canada*, (3), **23**. 159, 1929.

§ 4. The Chemical Reactions of Tellurium

In agreement with the general observation that the basic properties of the natural families of elements increase with rising atomic weight tellurium exhibits a greater basicity than selenium and sulphur. Sulphur is decidedly an acidic element, the acid character is weaker with selenium, and weaker still with tellurium. The last-named element exhibits feeble basic qualities since it forms a tartrate, basic sulphite and basic nitrate, and in this respect it exhibits the characters of a metal. Tellurium also resembles metal in general appearances. Lord Rayleigh and W. Ramsay,[1] and F. Fischer and F. Schrötter were unable to form a compound of **argon** and tellurium. According to H. Davy, F. Becker, J. Löwe, E. Priwoznik, F. Jones, M. G. Weber, and B. Brauner when tellurium is distilled in **hydrogen** a little tellurium hydride is formed; but A. Gutbier said that this is not the case with purified tellurium. A. Ditte observed that tellurium hydride is formed if tellurium be heated with hydrogen in a sealed tube. J. J. Berzelius said that crystalline tellurium does not change in **air,** but precipitated tellurium, when dried in air, is slightly oxidized, while B. Brauner, M. Berthelot and C. Fabre, and A. Gutbier found that a slight oxidation occurs during the washing of precipitated tellurium; and tellurium can be detected in the runnings from the filter; if allowed to stand exposed to air in the presence of hydrochloric acid, much tellurium tetrachloride passes into soln. J. J. Berzelius said that tellurium, heated in air somewhat above its m.p., burns with a bright blue flame which is green at the edges. The flame is attended by a white cloud of the oxide, which, according to J. J. Berzelius, and H. G. Magnus, has a faint unpleasant odour different from that of selenium; the horse-radish oxide reported by M. H. Klaproth is attributed to the presence of admixed selenium. H. B. Baker and H. B. Dixon observed that tellurium is one of the few elements which will burn in thoroughly dried **oxygen.** A. Mailfert said that in the presence of water **ozone** oxidizes tellurium to telluric acid. C. F. Cross and A. F. Higgin said that **water** does not act on tellurium either at ordinary temp. or when heated in a sealed tube at 160°. H. V. Regnault also found that tellurium does not decompose water at a red-heat. L. J. Thénard observed that **hydrogen dioxide** does not act on tellurium; but A. Gutbier and F. Resenscheck found that a soln. of the element in potash-lye is oxidized to tellurate. G. Schluck found that colloidal tellurium is acted on by very dil. soln. of the dioxide, whilst the crystalline modification only reacts slowly with 60 per cent. hydrogen dioxide at 100°. The rate of dissolution increases with the amount of telluric acid formed. Amorphous tellurium, precipitated from hydrochloric acid soln. by sulphur dioxide and dried at 105°, behaves similarly to crystalline tellurium, but if the amorphous variety is dried by treatment with alcohol and ether, it dissolves quite readily in conc. hydrogen dioxide soln. P. Köthner observed that an aq. soln. of **sodium dioxide** converts tellurium into the trioxide which dissolves as tellurate.

H. Moissan found that **fluorine** reacts with tellurium with incandescence forming a crystalline fluoride. H. Davy said that tellurium burns to the tetrachloride in **chlorine.** H. Rose found that chlorine does not attack powdered crystalline tellurium in the cold; but when feebly warmed, a reaction sets in with incandescence forming tellurium di- or tetrachloride according as the tellurium or the chlorine is in excess. On the other hand, J. Thomsen said that chlorine reacts slowly with tellurium at ordinary temp., and if a little sulphur be present, the reaction is faster. C. Willgerodt studied tellurium as a catalyst—*chlorüberträger*—in the chlorination of organic compounds. J. J. Berzelius found that **bromine** reacts with tellurium at ordinary temp., with the disengagement of heat, forming a bromide; tellurium and **iodine** can be melted together in any proportions; and if a mixture is heated strongly enough tellurium iodide sublimes. O. Ruff and H. Krug showed that tellurium reacts with incandescence with **chlorine fluoride.** W. Engelhardt observed that colloidal tellurium readily reacts with a soln. of iodine and potassium iodide. J. Thomsen said that **hydrochloric acid** is without action on tellurium. According to V. Lenher, although tellurium is ordinarily considered to be insoluble in hydrochloric acid, yet it is actually attacked slightly by the acid when exposed to the air, if sufficient time is allowed for contact. This action can be demonstrated by bubbling a current of air, for several weeks, through conc. hydrochloric acid in which is suspended metallic tellurium. In a comparatively short time the acid becomes yellow, indicating the presence of tetrachloride.

J. J. Berzelius said that **sulphur** can be melted with tellurium in all proportions—*vide infra*, tellurium sulphide. R. Weber, and E. Divers and M. Shimose observed that dry **sulphur dioxide** reacts with tellurium at 30° forming red tellurium sulphotrioxide. F. J. Müller von Reichenstein, and M. H. Klaproth, N. W. Fischer, H. G. Magnus, and H. Rose, and E. Divers and M. Shimose found that conc. or fuming **sulphuric acid** dissolves tellurium at ordinary temp. forming a red soln.; and, according to N. W. Fischer, with the conc. acid, sulphur dioxide is evolved. Tellurium separates out when water is added to the soln., and when heated, sulphur dioxide is evolved. The colour of the soln., said R. Weber, is probably due to the formation of tellurium sulphotrioxide. M. G. Levi and co-workers found that a soln. of potassium persulphate dissolves tellurium; E. Moles found that tellurium reacts with sulphuric acid giving a soln. with an increased conductivity, and hence mol. wt. determinations are ambiguous. According to R. Auerbach, tellurium in accord with its metallic character dissolves in **pyrosulphuric acid** as monatomic molecules, and in coagulation, the colour changes from red, through violet, to blue—*cf.* selenium oxysulphates. J. Thomsen said that tellurium vigorously decomposes **sulphur monochloride** forming tellurium tetrachloride; and this was shown by V. Lenher to occur when the monochloride is in excess, while F. Krafft and O. Steiner found that the dichloride is produced if the tellurium be in excess. W. Prandtl and P. Borinsky said that selenium or tellurium forms with **chlorosulphuric acid** an unstable soln. containing, respectively, $SeSO_3$ or $TeSO_3$; it reacts with **pyrosulphuryl chloride** to form $TeCl_4.SO_3$, in accord with the equation: $Te+2S_2O_5Cl_2=SO_3.TeCl_4+2SO_2+SO_3$; **chlorosulphonic acid** reacts: $Te+HClSO_3=HCl+TeSO_3$; and **sulphuryl chloride** is without action in the cold but forms the tetrachloride when heated, while B. von Horvath said that purified tellurium reacts at ordinary temp., and at a red-heat forms tellurium tetrachloride and sulphur dioxide; **thionyl chloride** yields the same products together with sulphur. V. Lenher also studied the action of sulphuryl and thionyl chlorides on tellurium. L. Tschugaeff and W. Chlopin found that in an atm. free from oxygen tellurium dissolves in sodium hydroxide containing **sodium hyposulphite** forming sodium telluride. J. J. Berzelius observed that **selenium** and tellurium can be melted together in all proportions, and heat is at the same time evolved—*vide supra*. C. A. Cameron and J. Macallan found that **selenic acid** dissolves tellurium in the cold forming a red soln. which is decomposed by water with the separation of tellurium; the red substance is probably tellurium selenotrioxide.

G. Gore, E. C. Franklin and C. A. Kraus, and C. Hugot found that tellurium is unchanged by liquid **ammonia.** F. W. Bergstrom found that tellurium reacts fairly quickly with the **amides** of potassium and sodium at ordinary temp., and slowly at −33°. C. A. Kraus discussed the complex anions formed by tellurium in ammonia soln. C. C. Palit and N. R. Dhar observed that 13 and 26 per cent. **nitric acid** exert but a slight action on tellurium in 3 hrs. According to A. Oppenheim, when a mixture of **phosphorus** and powdered tellurium is warmed, part of the tellurium forms a black compound, and part burns to phosphorus oxide. V. Lenher observed that **phosphorus trichloride,** and **phosphoryl trichloride** are without action on tellurium. J. J. Berzelius, and A. Oppenheim said that tellurium and **arsenic** can be melted together in all proportions; and similarly with **antimony** or **bismuth.** F. Jones found that **arsine** is converted by tellurium into arsenic telluride and hydrogen telluride; and **stibine** behaves in an analogous manner. J. Hoffmann observed no characteristic coloration is produced by tellurium in molten **borax;** the tellurium is sparingly dissolved, and forms a regulus. On the other hand, sodium telluride colours the molten borax brown or black. Molten **boric acid** dissolves some telluride and when cold the mass is brown; with fused **microcosmic salt,** and sodium telluride, a reddish-brown glass is formed, which, on the addition of boric oxide, becomes amber-yellow. P. Fenaroli found that, as in the case of selenium, the oxidized element does not colour **glass,** but if reducing conditions are present blue, brown, and red glasses are produced. Some contain colloidal soln. of the element, and others, polytellurides. The former correspond completely with the tellurium hydrosols, and are, like them, of two fundamental colours, blue and brown, analogous to the red selenium glass. The blue glass contains larger colloidal particles than the brown. The glass containing polytellurides is red, or violet-red, and has an absorption spectrum which corresponds exactly with that of aq. soln. of polytellurides, showing an absorption from the green to the violet, with a distinct maximum between 480 and 490$\mu\mu$.

J. W. Retgers found that tellurium is not dissolved by **benzene,** or **xylene;** and with **methylene iodide** it forms a dark brown soln.—100 parts of the solvent dissolve 0·1 part of tellurium at 12°. W. Muthmann said that the methylene iodide dissolves tellurium only when the liquid contains a little free iodine, but this was contradicted by J. W. Retgers. A. Gutbier added that tellurium decomposes the methylene iodide and passes into soln. as tellurium iodide. A. Oppenheim's observations on the action of a soln. of **potassium cyanide** have been discussed in connection with the separation of this element from selenium and sulphur. V. Lenher observed that **carbon tetrachloride** does not react with tellurium; and K. Lindner and L. Apolant found that when tellurium is heated with **carbonyl chloride,** tellurium dichloride is formed. H. Wayts and G. Cosyno studied the action of tellurium on organo-magnesium compounds. A. C. Vournasos found that when heated with **sodium formate,** tellurium hydride is formed. J. Dean studied some organic compounds of tellurium.

The action of tellurium on the **metals** is indicated in connection with the tellurides. According to M. le Blanc, when tellurium is heated with a N-soln. of **potassium hydroxide,** while protected from air, no action occurs at ordinary temp. or at 100°; but with a 10N-soln., the liquid becomes blood-red and the dissolved tellurium is precipitated when the soln. is diluted. H. Rose observed the formation of tellurides when tellurium is melted with alkali hydroxide; and J. J. Berzelius observed a similar result with **alkali carbonate.** M. Websky said that when tellurium is fused with **potassium hydrosulphate,** tellurium dioxide, or potassium tellurite is formed; and F. Becker found that fused **potassium nitrate** forms alkali tellurate; and similarly also with a fused mixture of potassium hydroxide and chlorate—*vide* the tellurates. Tellurium acts as a reducing agent on many salts of the heavy metals. Thus, J. B. Senderens obtained a partial reduction of **copper sulphate or acetate,** and he represented the reaction of powdered tellurium with **silver nitrate** at 100° by $4AgNO_3+3Te+3H_2O=2Ag_2Te+H_2TeO_3+4HNO_3$. In sealed tubes, the precipitation of the silver by tellurium is always complete, and if the tellurium is in excess, the nitric acid which is formed is decomposed with production of nitrogen peroxide even in dil. soln. Silver nitrate in soln. is completely although slowly reduced by selenium and tellurium at the ordinary temp. R. D. Hall and V. Lenher, and F. Hundeshagen, represented the action on **gold chloride** by $4AuCl_3+3Te=3TeCl_4+4Au$. Selenium reduced a soln. of gold chloride only when boiled; so that tellurium is a more active reducing agent than selenium. R. Böttger found that **ferric salts**—sulphate, ferrocyanide, etc.—are reduced to ferrous salts. F. W. Bergstrom found that tellurium failed to react with magnesium, arsenic, or copper in liquid ammonia, but did dissolve very slowly in soln. of aluminium and potassium cyanides. Evaporation of these soln. to dryness appeared to cause decomposition into cyanide and elementary tellurium. No definite compounds were isolated. Arsenic failed to react with soln. of potassium or aluminium cyanides over a long period of time. E. Kessler, and A. Gutbier and co-workers studied the purple substance, analogous to purple of Cassins, produced by the deposition of tellurium on **stannic hydroxide**—that is, *tellurium-tin purple.* H. Lessheim and co-workers discussed the co-ordination number of tellurium in its complex salts.

Some reactions of analytical interest.—As in the case of selenium, tellurium forms two acids—tellurous and telluric acids. When a soln. of a tellurite is treated with **hydrochloric acid,** a white precipitate of tellurous acid, H_2TeO_3, may be formed

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in conc. soln.; with a soln. of a tellurate, there is no precipitation, but if the soln. be boiled, chlorine is evolved, and when water is added, tellurous acid may be precipitated. Acidic soln. of a tellurite yield a brown precipitate of tellurium sulphide, TeS_2, when treated with **hydrogen sulphide,** and the precipitate is soluble in ammonium sulphide soln.; under similar conditions the tellurates behave like the tellurites to which they are reduced. As previously indicated—*vide* Figs. 1 and 2 of the previous chapter—**sulphur dioxide** precipitates tellurium completely from dil. hydrochloric acid soln., and this even in the presence of tartaric acid; but with a conc. hydrochloric acid soln., unlike selenious acid, no tellurium is precipitated even on boiling. Tellurous and telluric acids give similar products when treated with reducing agents—**stannous chloride** precipitates black tellurium if the soln. be not too acid; **zinc** gives a similar precipitate; **phosphorous acid** precipitates tellurium from conc. soln., but not from cold, dil. soln.; and **ferrous sulphate** gives no precipitate with tellurous or telluric acids although with the selenium acids precipitation occurs.

According to P. Jannasch,[2] an ammoniacal soln. of **hydroxylamine** reduces tellurous and telluric acids causing the complete precipitation of the tellurium, whilst an acidic soln. of this reagent is without action on these acids; hydroxylamine may therefore be employed in separating selenium and tellurium. The selenium is completely precipitated when a hydrochloric acid soln. of these elements is boiled with hydroxylamine, and the tellurium separates quantitatively when the filtrate is rendered ammoniacal and boiled with more of the reducing agent; four mols. of hydroxylamine are required for the reduction of one mol. of tellurous acid, water and nitrogen being produced at the same time. Tellurium is also precipitated from its hydrochloric acid soln. by **hydrazine sulphate,** but not from its soln. in nitric acid; hydrazine precipitates tellurium quantitatively from a hot ammoniacal soln. G. Pellini said that a feebly acidic soln. of selenium containing ammonium tartrate gives a precipitate with hydrazine sulphate, but not so with tellurium; hydrazine chloride precipitates both selenium and tellurium. For the action of other reducing agents—*vide infra*, tellurous and telluric acid. With magnesia mixture, tellurites give a white precipitate; so also with sodium hypophosphate, and with barium chloride. G. Denigès [3] found that a soln. of 10 grms. of **mercurous nitrate** in 10 c.c. of nitric acid and 100 c.c. of water gives a yellow crystalline precipitate with telluric acid or tellurates. If a tellurium compound or tellurium be melted with **potassium cyanide** in a current of hydrogen, potassium telluride is formed. When the cold mass is dissolved in water, and a current of air passed through the soln., unlike the case with selenium, the element itself is precipitated.

The physiological action of tellurium.—Soln. of the tellurium salts have a metallic taste; and, according to K. Hansen,[4] and A. P. A. Rabuteau, they are poisonous. B. Turina found that like selenium salts, tellurium—as tellurite or tellurate—does not enter the system of germinating or mature plants in appreciable quantities by way of the root-hairs; rather does the root-sap play the important rôle of point of entry and filtration for nutrifying salts. F. Czapek and J. Weil said that in the organism tellurium salts are rapidly reduced to the metallic state, which is harmless. F. Wöhler, K. Hansen, F. Mylius, and J. L. Beyer were of the opinion that a small quantity of telluric or tellurous acid—say, 1 mgrm.—taken internally is reduced to tellurium simultaneously forming a volatile compound—possibly methyl telluride—which imparts to the breath a most offensive odour. F. Lehmann said that high concentrations of tellurium salts are fatal to trypanosomes, but after one hour's exposure, the following dilutions were not lethal: tellurites 1 : 500; and tellurates 1 : 300. G. Joachimoglu and W. Hirose observed that on an isolated frog's heart, sodium tellurite is at least two hundred times as toxic as sodium tellurate, and sodium selenite at least one hundred times as toxic as sodium selenate. The selenite is also much more toxic than the tellurite. The heart muscalature has a reducing effect on the first three salts mentioned.

On the rabbit's blood-press., sodium selenite and tellurite have a more powerful depressor action than sodium selenate and tellurate. They also showed that diphtheria bacilli are less sensitive than the bacilli of the typhus-coli group towards tellurites and tellurates. The former are killed by conc. of tellurites 1 : 420, and tellurates 1 : 125—while the latter are killed at dilutions 400 times these amounts. According to A. Massen, the solid compounds of selenium and tellurium are attacked by *Penicillium brevicaule*, forming volatile substances. The volatile selenium compound has a mercaptan-like odour, quite distinct from that of the arsenic compound, but cultures containing tellurium emit an odour resembling that of garlic. Whilst in the animal organism selenium and tellurium compounds are converted into ethyl derivatives, in microbes, methyl derivatives are formed. The reducing property of the cells of animals and microbes is due to the presence of a substance which can exercise this power even when removed from the tissues, but the formation of methyl or ethyl derivatives seems, however, to be really dependent on vital processes occurring only in the organism. O. Rosenheim, and A. Massen discussed the effects of the presence of selenium and tellurium on the biological tests for arsenic. B. Gosio added that whilst all arsenical compounds are attacked only by a comparatively few species of hyphomycetes; only some of tellurium compounds are attacked by all the varieties of hyphomycetes tried. The action with the tellurium compounds is more rapid than with arsenical compounds, and under favourable conditions can be detected in 2 or 3 min. It is said to be probable that the decomposition of tellurium compounds by micro-organisms is not brought about by means of products formed by the organisms, but is a direct consequence of the life or development of the moulds or bacteria. B. Gosio, and E. Scheurlen recommended the use of tellurium compounds as tests for bacterial life in substances supposed to have been sterilized. L. D. Mead and W. J. Gies found that non-toxic doses of tellurium (as oxide, tellurite, tartrate, and tellurate) do not materially affect metabolism in dogs. They appear to stimulate katabolism, and diminish fat absorption slightly; the urine is rendered dark brown. Large doses retard digestion, and induce vomiting and somnolence. They cause enteritis. Subcutaneously injected, they cause diarrhœa, tremors, and death from asphyxia. At the point of injection, tellurium is deposited in the metallic form, and is distributed in most of the organs and tissues. Methyl telluride appears in the breath a few minutes after the introduction of quite small amounts of tellurium into the system. It persists for months, slowly leaving the body, by skin, lungs, urine, bile, and fæces. Of the digestive ferments, trypsin is the least resistive to the destructive influence of the metal. Albumin and bile pigment are usually present in the urine. T. Bokorny said that a 0·1 per cent. aq. soln. of telluric acid, or of potassium tellurite or tellurate, has no action on various algæ and infusoria. W. Adolphi described a case of poisoning from the fumes of tellurous oxide volatilized during the smelting of some platinum slimes. N. M. Stover and B. S. Hopkins found that sodium or potassium tellurite, or tellurium acid tartrate in 0·0005N- to 0·05N-soln., exert no perceptible fungicidal action.

Some uses of tellurium compounds.—On account of some industrial applications, tellurium is beginning to acquire some technical importance.[5] It has a very limited application in the glass industry; it is used in the preparation of organic dye-stuffs; in the manufacture of electrical equipment; high resistance alloys and ultramarine; in the colouring of lithophone; the staining of silver; as a delicate test of sterilization in bacteriology; and as a toning agent in photography. A compound of tellurium has been used as an anti-knock constituent of motor fuels, and its use is said to lead to greater efficiency. Remarkable properties are shown by the alloys of tellurium; the tin alloys are extremely hard and have very great tensile strength; and the aluminium alloys are very ductile. The silver alloys have been used. The element is poisonous, and is fairly readily absorbed—*e.g.* from gold dental stoppings. F. C. Mathers and J. Papish used soln. of salts of tellurium for staining metals; C. Dickens used colloidal tellurium as an insecticide, germicide, fungicide, and wood preservative.

References.

[1] J. Löwe, *Sitzber. Akad. Wien*, **10**. 727, 1853; *Journ. prakt. Chem.*, (1), **60**. 163, 1853; E. Priwoznik, *Vorkommen von Tellur und Gewinnung aus seinen Erzen*, Wien, 1893; *Oesterr. Zeit. Berg. Hütt.*, **45**. 219, 1895; B. Brauner, *Journ. Chem. Soc.*, **55**. 382, 1889; **67**. 527, 549, 1895; *Sitzber. Akad. Wien*, **98**. 456, 1889; *Monatsh.*, **10**. 413, 1887; **12**. 34, 1891; J. J. Berzelius, *Schweigger's Journ.*, **6**. 311, 1812; **34**. 78, 1823; *Pogg. Ann.*, **8**. 411, 1826; **28**. 392, 1833; **32**. 1, 577, 1834; F. J. Müller von Reichenstein, *Phys. Arb. Freunde Wien*, **1**. 1, 1782; **3**. 48, 1785; A. Gutbier, *Studien über das Tellur*, Leipzig, 1901; *Zeit. anorg. Chem.*, **32**. 31, 1902; K. Lindner and L. Apolant, *ib.*, **136**. 381, 1926; A. Gutbier and F. Resenscheck, *ib.*, **160**. 48, 1927; E. Kessler, *Selen- und Tellur-purpur*, Jena, 1927; H. Lessheim, J. Meyer and R. Samuel, *Zeit. anorg. Chem.*, **165**. 253, 1927; W. Muthmann, *ib.*, **10**. 218, 1895; J. W. Retgers, *ib.*, **3**. 349, 1893; **12**. 114, 1896; W. Prandtl and P. Borinsky, *ib.*, **52**. 237, 1909; P. Borinsky, *Ueber die Einwirkung von Schwefeltrioxyd und dessen Chlorosubstitutionsprodukten auf Schwefel, Selen und Tellur*, München, 1909; B. von Horvath, *Zeit. anorg. Chem.*, **70**. 408, 1911; H. V. Regnault, *Ann. Chim. Phys.*, (3), **2**. 62, 1836; M. Berthelot and C. Fabre, *ib.*, (6), **14**. 92, 1887; H. Moissan, *ib.*, (6), **24**. 239, 1896; L. J. Thénard, *Traité de chimie*, Paris, **8**. 478, 1816; **2**. 69, 1824; H. B. Baker and H. B. Dixon, *Proc. Roy. Soc.*, **45**. 1, 1888; H. B. Baker, *Phil. Trans.*, **179**. 571, 1888; C. F. Cross and A. F. Higgin, *Journ. Chem. Soc.*, **35**. 177, 1879; E. Divers and M. Shimose, *ib.*, **43**. 319, 323, 329, 1883; A. Mailfert, *Compt. Rend.*, **94**. 1186, 1882; J. B. Senderens, *ib.*, **104**. 175, 1887; J. Margottet, *Ann. École Norm.*, **8**. 247, 1879; *Recherches sur les sulfures, les séléniures, et les tellurures métalliques*, Paris, 1879; *Compt. Rend.*, **84**. 1293, 1877; A. Ditte, *ib.*, **74**. 984, 1872; H. G. Magnus, *Dissertatio de tellurio*, Berolensis, 1827; *Pogg. Ann.*, **17**. 521, 1829; M. H. Klaproth, *Mem. Akad. Berlin*, **50**. 17, 1798; *Beiträge zur chemischen Kenntniss der Mineralkörpen*, Berlin, **3**. 1, 1802; London, **2**. 1, 1804; *Crell's Ann.*, **1**. 91, 1798; *Gilbert's Ann.*, **12**. 246, 1802; H. Davy, *Phil. Trans.*, **100**. 231, 1810; H. Rose, *Pogg. Ann.*, **21**. 443, 1831; N. W. Fischer, *ib.*, **10**. 491, 1827; **12**. 153, 1828; **114**. 328, 1828; **15**. 77, 1829; **16**. 118, 1829; C. Willgerodt, *Journ. prakt. Chem.*, (2), **34**. 269, 1887; (2), **35**. 391, 1887; R. Weber, *ib.*, (2), **25**. 218, 1882; A. Oppenheim, *ib.*, (1), **71**. 278, 1837; R. Böttger, *ib.*, (2), **9**. 195, 1874; M. G. Weber, *Kristische Studien über die Darstellungsweisen von Selen- und Tellurwasserstoff*, Weida i. Th., 1910; J. Hoffmann, *Zeit. angew. Chem.*, **19**. 1089, 1906; J. Thomsen, *Ber.*, **15**. 3024, 1882; L. Tschugaeff and W. Chlopin, *ib.*, **47**. 1269, 1914; *Journ. Russ. Phys. Chem. Soc.*, **47**. 364, 1915; R. Auerbach, *Koll. Zeit.*, **38**. 343, 1926; *Zeit. phys. Chem.*, **121**. 337, 1926; R. D. Hall and V. Lenher, *Journ. Amer. Chem. Soc.*, **24**. 918, 1902; V. Lenher, *ib.*, **24**. 118, 1902; **30**. 737, 1908; F. W. Bergstrom, *ib.*, **48**. 2319, 1926; C. A. Kraus, *ib.*, **44**, 1216, 1922; F. Hundeshagen, *Chem. Ztg.*, **29**. 799, 1905; C. C. Palit and N. R. Dhar, *Journ. Phys. Chem.*, **30**. 1125, 1926; M. Websky, *Zeit. anal. Chem.*, **11**. 128, 1872; J. Dean, *The Organic Compounds of Tellurium and Selenium belonging to the Alcohol Series*, Göttingen, 1855; M. le Blanc, *Zeit. Elektrochem.*, **12**. 649, 1906; P. Köthner, *Das reine Tellur. Sein Atomgewichte*, Halle, 1901; *Liebig's Ann.*, **319**. 1, 1901; F. Becker, *ib.*, **180**. 259, 1876; G. Gore, *Proc. Roy. Soc.*, **20**. 441, 1872; **21**. 140, 1873; C. A. Cameron and J. Macallan, *ib.*, **46**. 31, 1889; *Chem. News*, **59**. 219, 432, 258, 269, 1889; E. C. Franklin and C. A. Kraus, *Amer. Chem. Journ.*, **20**. 820, 1878; F. Jones, *Proc. Chem. Soc.*, **23**. 164, 1907; *Mem. Manchester Lit. Phil. Soc.*, **48**. 16, 1904; C. Hugot, *Compt. Rend.*, **121**. 206, 1895; P. Fenaroli, *Chem. Ztg.*, **38**. 273, 1914; *Koll. Zeit.*, **16**. 53, 1915; E. Moles, *Acad. Fis. Quim.*, **13**. 134, 1915; G. Schluck, *Monatsh.*, **37**. 489, 1916; F. W. Bergstrom, *Journ. Phys. Chem.*, **30**. 12, 1926; F. Krafft and O. Steiner, *Ber.*, **34**. 560, 1901; O. Steiner, *Beiträge zur Kenntniss der Schwefel-Selen-Tellur-Gruppe*, Heidelberg, 1900; H. Wayts and G. Cosyno, *Bull. Soc. Chim.*, (3), **29**. 689, 1903; A. C. Vournasos, *Ber.*, **43**. 2272, 1910; M. G. Levi, E. Migliorini and G. Ercolini, *Gazz. Chim. Ital.*, **38**. i, 598, 1908; Lord Rayleigh and W. Ramsay, *Phil. Trans.*, **186**. A, 231, 1895; *Proc. Roy. Soc.*, **57**. 282, 1895; *Chem. News*, **71**. 57, 1895; F. Fischer and F. Schrötter, *Ber.*, **43**. 1442, 1910; W. Engelhardt, *Koll. Zeit.*, **45**. 42, 1928; O. Ruff and H. Krug, *Zeit. anorg. Chem.*, **190**. 270, 1930.

[2] P. Jannasch, *Ber.*, **31**. 2377, 1898; G. Pellini, *Gazz. Chim. Ital.*, **30**. i, 515, 1903.

[3] G. Denigès, *Ann. Chim. Anal.*, **20**. 57, 1915.

[4] K. Hansen, *Journ. Pharm. Chim.*, (3), **24**. 238, 1853; *Liebig's Ann.*, **86**. 208, 1853; F. Czapek and J. Weil, *Arch. Exp. Pathol.*, **32**. 438, 1894; A. P. A. Rabuteau, *Ann. Chim. Phys.*, (6), **10**. 121, 1887; E. Scheurlen, *Zeit. Hyg.*, **33**. 135, 1900; F. Wöhler, *Pogg. Ann.*, **11**. 161, 1827; G. Joachimoglu, *Zeit. Urol.*, **16**. 97, 1922; G. Joachimoglu and W. Hirose, *Biochem. Zeit.*, **125**. 1, 5, 1921; B. Turina, *ib.*, **129**. 507, 1922; F. Lehmann, *ib.*, **134**. 390, 1922; N. M. Stover and B. S. Hopkins, *Journ. Ind. Eng. Chem.*, **19**. 510, 1927; F. Mylius, *Ber.*, **34**. 2219, 1901; T. Bokorny, *Chem. Ztg.*, **17**. 1598, 1893; W. Adolphi, *ib.*, **46**. 722, 1922; A. Massen, *Arb. Kaiser. Ges. Amt.*, **18**. 475, 1902; O. Rosenheim, *Proc. Chem. Soc.*, **18**. 138, 1902; L. D. Mead and W. J. Gies, *Amer. Journ. Physiol.*, **3**. 20, 1900; **5**. 104, 1901; B. Gosio, *Atti Accad. Lincei*, (5), **13**. i, 422, 1904; (5), **14**. ii, 188, 1905; J. L. Beyer, *Arch. Physiol.*, 225, 1895.

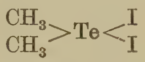
[5] Anon., *Chem. Trade Journ.*, **79**. 309, 1926; H. A. Doermer, *Rept. Investigations—Bur. Mines*, 2385, 1922; V. Lenher, *Trans. Amer. Inst. Min. Met. Eng.*, **69**. 1035, 1923; *Chem. Met.*

Engg., **22**. 1100, 1920; *Journ. Ind. Eng. Chem.*, **12**. 597, 1920; F. C. Mathers and J. Papish, *U.S. Pat. No.* 1308092, 1919; C. Dickens, *ib.*, 1536379, 1925; *Chem. Met. Engg.*, **32**. 413, 1925; H. A. Doermer, *Journ. Franklin Inst.*, **194**. 409, 1922; C. M. Dyson, *Chem. Age*, **19**. 17, 1928.

§ 5. The Atomic Weight and Valency of Tellurium

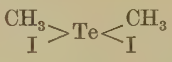
> Le tellure a donc subi toutes les tortures auxquelles un corps peut être soumis. Il a été fondu, sublimé, oxyde, hydrogéné, dissous et précipité, mais, le nombre 125, représentant le poids atomique de tellure pur, inscrit dans son tableau périodique par Mendeléeff, n'a été, jusqu'ici, confirmé par personne.—G. N. WYROUBOFF.

Tellurium shows a clear and definite relationship to selenium and to sulphur. This is evidenced by the valencies as shown by corresponding compounds. Thus, tellurium is bivalent in tellurium dichloride, $TeCl_2$, hydrogen telluride, H_2Te, the organic tellurides—*e.g.* ethyl telluride, $(C_2H_5)_2Te$, prepared by A. Marquardt and A. Michaelis[1]—and the inorganic tellurides—*e.g.* Ag_2Te, etc. According to F. Becker, and A. Cahours the organic tellurides form additive compounds with the alkyl iodides yielding the so-called *telluronium salts*—*e.g.* triethyl telluronium iodide, $(C_2H_5)_3TeI$, in which the tellurium is quadrivalent. There are also compounds like diethyl tellurium oxide, $(C_2H_5)_2TeO$, and the salts $(C_2H_5)_2TeCl_2$, etc., in which the tellurium is also quadrivalent. According to G. Pellini, $(C_6H_5)_2TeBr_2$ is isomorphous with the corresponding selenium compound $(C_6H_5)_2SeBr_2$. According to T. M. Lowry, the tetrahedral configuration of the sulphur and selenium does not apply to tellurium since R. H. Vernon has isolated two stereoisomeric forms of E. A. Demarçay's dimethyl telluronium diiodide:



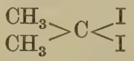
$\begin{matrix}CH_3\\CH_3\end{matrix}>Te<\begin{matrix}I\\I\end{matrix}$

and



$\begin{matrix}CH_3\\I\end{matrix}>Te<\begin{matrix}CH_3\\I\end{matrix}$

The isomerism is best explained on the assumption that the four valencies of tellurium lie in one plane. In these compounds, two of the valencies of tellurium appear to be different from the other two, whereas with sulphur and selenium, one valency appears to be different from the other three. Hence, the same argument which indicates that the four radicles of isopropylidene iodide



$\begin{matrix}CH_3\\CH_3\end{matrix}>C<\begin{matrix}I\\I\end{matrix}$

are not coplanar shows that the four radicles in the analogous compounds of tellurium have a square not a tetrahedral configuration. The subject was discussed by R. F. Goldstein, and by T. M. Lowry and co-workers. The quadrivalency of tellurium is also illustrated by tellurium tetrachloride, $TeCl_4$, which, according to A. Michaelis, has a normal vap. density, and passes into tellurous acid, $TeO(OH)_2$, when treated with water. The sexivalency of tellurium is represented by the hexafluoride, TeF_6, prepared by E. B. R. Prideaux, but not so clearly in telluric acid, known only in the form of the dihydrate, $H_2TeO_4.2H_2O$, which may be orthotelluric acid, $Te(OH)_6$, and in the tellurates which have a formal resemblance to the selenates and sulphates. The isomorphism of these salts has been previously discussed. I. I. Tschernyeff discussed the constitution of the complex salts; and J. N. Frers, the place of tellurium in the periodic table.

According to the periodic law, tellurium should have an at. wt. between that of antimony and iodine—that is, it should be greater than 120, and less than 126. J. J. Berzelius[2] gave 128 for the at. wt. of tellurium, while iodine has an at. wt. very near to 126·5. D. I. Mendeléeff accepted 125 for the at. wt. based, he said, on the work of B. Brauner; but this value for the at. wt. of tellurium is too low; all the best determinations agree that the at. wt. of tellurium is above that of iodine. This means that either all the observations are affected by a constant error, or else the theory is insufficient to describe the facts.

B. Brauner said that tellurium is not a simple substance, because on distilling tellurium in a current of hydrogen, or the tetrabromide, in vacuo, it can be separated into two constituents, one more volatile than the other, and having a different at. wt. He added that as a result of fractional precipitation with ammonia, tellurium as ordinarily understood is probably a mixture of three elements, and that pure, red tellurium remains to be discovered. P. E. Browning and R. Flint also said that if purified tellurium tetrachloride be partially hydrolyzed by water, and the precipitated tellurium dioxide separated by filtration the tellurium has an at. wt. of 126·53 ; whereas the tellurium salt remaining in soln., when precipitated by ammonia and a slight excess of acetic acid, contains tellurium which has an at. wt. of 128·97. They called the former *α-tellurium*, and the latter β-tellurium. These results were subsequently confirmed by R. Flint. G. Pellini suggested that tellurium contains a small quantity of an element of at. wt. 212, apparently corresponding with D. I. Mendeléeff's *di-tellurium*, Dt, which B. Brauner called *austriacum*, and which is said to be analogous to the radioactive constituents of pitchblende. W. Grünewald said that his spectroscopic observations on tellurium agree with the assumption that a dwi-tellurium was present. E. W. Wetherell asked :

> May it not be possible that the atoms of an element may in some cases have a satellite —a minute body inseparable from the atom by any means at our disposal, yet one which may materially affect the properties of an element ? Such satellite would in no way upset the law of Avogadro that equal vols. of a gas under equal press. and temp. contain equal numbers of molecules, as the satellite is an integral part of the molecule ; it might even account for the very slight deviation from the law which has been observed.

These speculations and observations have not been supported by others, and this in spite of a bias, so to speak, in favour of the heterogeneity of tellurium. A. G. V. Harcourt and H. B. Baker attributed the results by P. E. Browning and R. Flint to the failure of the methods of purification to remove some element of lower eq. wt. than tellurium, and that this impurity accumulated by the process of fractionation employed. A. G. V. Harcourt and H. B. Baker were unable to confirm R. Flint's results. W. G. Morgan, and G. Pellini obtained results in agreement with those of A. G. V. Harcourt and H. B. Baker, and opposed to those of R. Flint. W. Marckwald believed that by a laborious fractional crystallization of telluric acid, he obtained tellurium of lower at. wt. than that of iodine, but on repeating the work by a more trustworthy process, W. Marckwald and A. Foizik concluded that no separation of the tellurium had been effected. L. Staudenmaier fractionally crystallized telluric acid ; J. F. Norris and co-workers fractionally crystallized potassium bromotellurate ; J. F. Norris fractionally distilled tellurium dioxide ; H. B. Baker and A. H. Bennett fractionally crystallized telluric acid, fractionally dissolved barium tellurate, and fractionally distilled the metal, the chloride, and the dioxide, fractionally decomposed the hydride, fractionally precipitated the chloride, and fractionally electrolyzed the bromide and the chloride ; V. Lenher fractionally precipitated the tetrachloride or complex chlorides ; fractionally precipitated the tetrachloride with ferrous salts, and fractionally dissolved tellurium in hydrochloric acid in the presence of air. W. L. Dudley and P. C. Bowers fractionally precipitated tellurium by a hydrazine salt ; O. Steiner, and G. Pellini fractionally distilled phenyl telluride ; and G. Pellini fractionally hydrolyzed the tetrachloride, and fractionally electrolyzed a soln. of tellurium dioxide in sulphuric acid and ammonium hydrotartrate. In all cases, these investigators were unable to distinguish any difference in the at. wts. of the different fractions, and they concluded that tellurium is chemically homogeneous ; *i.e.* if tellurium is a mixture the components cannot be separated by the processes so far investigated. The differences observed by W. Bettel in the cupellation of silver telluride ores were attributed by H. B. Baker to differences in the surface tensions of silver telluride and silver ; and have no bearing on the controversy on the complexity of tellurium —*vide infra*, isotopes.

J. J. Berzelius [3] made the first attempt to determine the at. wt. of tellurium by oxidizing the element to the dioxide by means of nitric acid, and from the ratio

Te : TeO_2, he calculated 128·34 for the at. wt. when his data are reduced to oxygen 16 as the standard. W. L. Wills also obtained results ranging from 126·64 to 129·66 ; and a whole series of observations on the oxidation of tellurium to the dioxide, or the reduction of the dioxide to tellurium have been made. Thus, for the oxidation, B. Brauner obtained 125·72, and for the reduction, 127·46 ; G. Pellini obtained for the oxidation 127·657, and for the reduction, 127·625 ; G. Gallo found 127·053 ; V. Lenher, 127·50 ; A. Gutbier, 127·585, 127·609, and 126·74 ; L. Staudenmaier, 127·60 ; R. Metzner, 128·032 ; K. B. Heberlein, 127·002 ; L. M. Dennis and R. P. Anderson, 127·61 ; A. Stähler and B. Tesch, 127·513 ; and P. Bruylants and C. Desmet, 127·75. J. B. A. Dumas by an unpublished method obtained 129 for the at. wt. of tellurium.

C. von Hauer analyzed potassium bromotellurate, and from the ratio $K_2TeBr_6 : 6AgBr$, obtained 127·64 ; W. L. Wills from the same ratio obtained 127·10. B. Brauner obtained from the ratio TeBr : 4Ag, 127·64 ; M. Chikashige, 127·42 ; H. B. Baker and A. H. Bennett obtained from the ratio Te : $TeBr_4$, 127·53 (Br=74·92). W. L. Dudley and P. C. Bowers precipitated tellurium by a hydrazine salt and from the ratio $TeBr_4$: Te, calculated 127·479. V. Lenher obtained 127·57 from the ratio $K_2TeBr_6 : 2KCl$. L. Staudenmaier obtained 127·16 from the ratio $H_6TeO_6 : TeO_2$, and 127·31 from the ratio H_6TeO_6 : Te ; W. Marckwald gave 126·81 ; and K. B. Heberlein similarly obtained 126·72. H. B. Baker objected to telluric acid as a starting point because of the difficulty in obtaining the acid with exactly the right proportion of water of crystallization, $H_2TeO_4.2H_2O$. K. B. Heberlein treated telluric acid with hydrochloric acid, collected the liberated chlorine in potassium iodide, and titrated the freed iodine with standard thiosulphate ; he thus obtained Te=127·223. O. Steiner analyzed phenyl telluride, and from the ratio $(C_6H_5)_2Te : 12CO_2$ obtained Te=126·42 ; A. Scott from the ratio $(CH_3)_3TeI : AgI$ obtained 127·56 ; and from the ratio $(CH_3)_3TeBr : Ag$, 127·72. J. F. Norris ignited the basic nitrate, and from the ratio $Te_2HNO_7 : 2TeO_2$ obtained 127·48. W. L. Dudley and P. C. Bowers showed that the basic nitrate method is not so reliable owing to variations in composition with variations in the nature of the precipitate. H. B. Baker and A. H. Bennett heated tellurium dioxide with sulphur, and from the ratio $TeO_2 : SO_2$, obtained 127·62. W. Marckwald and A. Foizik said that the results by this process are not so good owing to the formation of a little sulphur trioxide. F. A. Gooch and J. Howland oxidized an alkaline soln. of tellurium dioxide to telluric acid by adding an excess of a standard soln. of permanganate, and after acidification with sulphuric acid, titrated back the excess with oxalic acid. They thus obtained 126·92 for the at. wt. of tellurium ; J. F. Norris and H. Fay determined the excess of permanganate iodometrically. W. Marckwald and A. Foizik also oxidized the tellurium dioxide to telluric acid by permanganate in an acidic or an alkaline soln. The results gave 127·61 for the at. wt. of tellurium. P. Bruylants and J. Michielsen calculated 127·8 from the ratio Te : H_2 in hydrogen telluride. G. Gallo found the electrochemical equivalent of tellurium in terms of silver, and he found that if the at. wt. of silver be 107·880, that of tellurium is 127·053.

The available data were reviewed by K. Seubert, and P. Köthner in 1903 ; and by F. W. Clarke in 1910. F. W. Clarke gave 127·5 as the best representative value for the at. wt. ; and the International Table for 1926, 127·5, and for iodine, 126·92. Tellurium is therefore considered to be a misfit in the periodic table of at. wts. As G. N. Wyrouboff,[4] and H. Wilde expressed it, the law of periodicity ceases to be valid. J. W. Retgers accordingly argued that tellurium should be placed in the eighth group, and he said, in support of this, that potassium tellurate and osmiate are isomorphous. On the other hand, W. Muthmann said that the general character of tellurium ; the isomorphism of potassium selenium bromide, and potassium tellurium chloride ; and the isomorphism of the trigonal forms of tellurium and selenium make tellurium fitted for a place in the periodic table along with sulphur and selenium. As indicated above, J. W. Retgers considered that the cases of isomorphism cited by W. Muthmann are open to doubt. In spite of this, the chemical characters alone, in the opinion of K. Seubert, make tellurium a member of the sulphur-selenium family; and, added A. Gutbier and F. Flury, the anomaly would not be avoided by placing tellurium in the eighth group away from its congeners sulphur and tellurium in the sixth group. A. Werner showed that the anomaly exhibited by tellurium is itself periodic and appears in other parts of the table—*e.g.* with argon (39·9) and potassium (39·15); with cobalt (59·0) and nickel (58·7); and with neodymium (143·6) and praseodymium (140·5). P. Kusnetzoff pointed out that when the differences in the at. wts. of the elements in the uneven periods are tabulated, they show a regular rise and fall within the separate groups. The negative difference between iodine and tellurium is in accord with the other differences in the sixth group.

The case of tellurium shows that the position of an element in the periodic table is not entirely dependent on its at. wt., but on some other property of the atom to which the at. wt. is nearly proportional. A. van den Broek [5] showed that if the elements are arranged in the order of their at. wts. they are in nearly all cases also arranged in the order of increasing nuclear charge; and it is the nuclear charge not the at. wt. which should determine the position of the element in the periodic table; and H. G. J. Moseley showed that the variation in the wave-length of the characteristic X-rays emitted by different elements can be explained on the assumption that the nuclear charge increases by one unit from element to element. The nuclear charge is represented by so-called **atomic number,** which for tellurium is 52.

The theory of isotopes has also changed the point of view of the at. wt. question. According to F. W. Aston,[6] the mass spectrum of tellurium gives lines corresponding with **isotopes** of the at. wts. 126, 128, and 130, the intensities of the latter two being equal and double that of the first. All the mass numbers of tellurium probably form members of isobaric pairs. H. Pettersson and G. Kirsch [7] observed evidence of **atomic disruption** when tellurium is bombarded by α-rays. H. Müller obtained no evidence of this. A. L. Foley studied the action of ultra-violet light; and of X-rays on tellurium confined in sealed glass tubes when the spectra are periodically examined. The results were indefinite. The **electronic structure** according to N. Bohr is (2) (4, 4) (6, 6, 6) (6, 6, 6) (4, 2). The subject was discussed by M. L. Huggins, G. I. Pokrowsky, C. P. Smyth, H. G. Grimm and A. Sommerfeld, J. D. M. Smith, J. C. Slater, and C. D. Niven.

Polonium is discussed in connection with radium.

References.

[1] A. Marquardt and A. Michaelis, *Ber.*, **21**. 2042, 1888; A. Michaelis, *ib.*, **20**. 2488, 1887; F. Becker, *Liebig's Ann.*, **180**. 263, 1876; A. Cahours, *Ann. Chim. Phys.*, (5), **10**. 50, 1877; G. Pellini, *Atti Accad. Lincei*, (5), **18**. ii, 279, 1909; E. B. R. Prideaux, *Journ. Chem. Soc.*, **89**. 322, 1906; G. N. Wyrouboff, *Les actualités chimiques*, **1**. 18, 1896; R. F. Goldstein, *Journ. Soc. Chem. Ind.—Chem. Ind.*, **44**, 1011, 1925; R. H. Vernon, *Journ. Chem. Soc.*, **117**. 86, 889, 1920; **119**. 105, 687, 1921; I. I. Tschernyeff, *Ann. Inst. Platin.*, 118, 1927; T. M. Lowry, R. R. Goldstein and F. L. Gilbert, *ib.*, 307, 1928; F. L. Gilbert and T. M. Lowry, *Nature*, **123**. 85, 1929; *Journ. Chem. Soc.*, 1907, 3179, 1928; 2076, 2867, 1929; G. T. Morgan and F. H. Burstall, *ib.*, 3260, 1928; G. T. Morgan and H. Burgess, *ib.*, 2215, 1929; T. M. Lowry and F. L. Gilbert, *ib.*, 2076, 1929; T. M. Lowry, *Journ. Soc., Chem. Ind.—Chem. Ind.*, **46**. 72, 102, 1927; E. A. Demarçay, *Bull. Soc. Chim.*, (2), **40**. 99, 1883.

[2] D. I. Mendeléeff, *Journ. Chem. Soc.*, **55**. 651, 1889; B. Brauner, *Monatsh.*, **10**. 413, 1889; *Sitzber. Akad. Wien*, **98**. 456, 1889; *Journ. Chem. Soc.*, **55**. 382, 1889; **67**. 549, 1895; H. B. Baker and A. H. Bennett, *ib.*, **91**. 1849, 1907; A. G. V. Harcourt and H. B. Baker, *ib.*, **99**. 130, 1911; H. B. Baker, *Chem. News*, **97**. 209, 1908; W. Bettel, *ib.*, **97**. 169, 1908; E. W. Wetherell, *ib.*, **90**. 260, 1904; J. J. Berzelius, *Pogg. Ann.*, **28**. 395, 1833; R. Flint, *Journ. Amer. Chem. Soc.*, **34**. 1325, 1912; *Amer. Journ. Science*, (4), **30**. 209, 1910; P. E. Browning and R. Flint, *ib.*, (4), **28**. 347, 1909; *Zeit. anorg. Chem.*, **64**. 112, 1909; J. F. Norris, H. Fay and D. W. Edgerly, *Amer. Chem. Journ.*, **23**. 105, 1900; J. F. Norris, *Journ. Amer. Chem. Soc.*, **28**. 1675, 1906; V. Lenher, *ib.*, **30**. 741, 1908; **31**. 20, 1909; W. G. Morgan, *ib.*, **34**. 1669, 1912; W. L. Dudley and P. C. Bowers, *ib.*, **35**. 375, 1913; G. Pellini, *Gazz. Chim. Ital.*, **32**. i, 131, 1902; **33**. ii, 35, 1903; *Atti Accad. Lincei*, (5), **21**. 1, 218, 1912; *Ber.*, **34**. 3807, 1901; W. Marckwald, *ib.*, **40**.

4730, 1897 ; W. Marckwald and A. Foizik, *ib.*, **43**. 1710, 1910 ; L. Staudenmaier, *Untersuchungen über das Tellur*, Leipzig, 1895 ; *Zeit. anorg. Chem.*, **10**. 189, 1895 ; J. W. Retgers, *ib.*, **12**. 98, 1896 ; *Zeit. phys. Chem.*, **12**. 596, 1893 ; O. Steiner, *Ber.*, **34**. 570, 1901 ; *Beiträge zur Kenntniss der Schwefel-Selen-Tellur-Gruppe*, Heidelberg, 1900 ; W. Grünewald, *Sitzber. Akad. Wien*, **98**. 785, 1889 ; J. M. Freres, *Zeit. anorg. Chem.*, **186**. 145, 1930.

[3] J. J. Berzelius, *Pogg. Ann.*, **28**. 395, 1833 ; C. von Hauer, *Sitzber. akad. Wien*, **25**. 142, 1857 ; *Journ. prakt. Chem.*, (1), **73**. 98, 1858 ; J. B. A. Dumas, *Ann. Chim. Phys.*, (3), **55**. 129, 1859 ; B. Brauner, *Monatsh.*, **10**. 413, 1889 ; *Sitzber. Akad. Wien*, **98**. 456, 1889 ; *Journ. Chem. Soc.*, **55**. 382, 1889 ; **67**. 549, 1895 ; W. L. Wills, *Liebig's Ann.*, **202**. 246, 1880 ; *Journ. Chem. Soc.*, **35**. 704, 1879 ; B. Brauner, *Monatsh.*, **10**. 411, 1889 ; *Zeit. anorg. Chem.*, **31**. 374, 1902 ; *Journ. Chem. Soc.*, **55**. 382, 1889 ; **67**. 549, 1895 ; M. Chikashige, *ib.*, **69**. 881, 1896 ; H. B. Baker and A. H. Bennett, *ib.*, **91**. 1849, 1907 ; A. G. V. Harcourt and H. B. Baker, *ib.*, **99**. 1311, 1911 ; H. B. Baker, *Chem. News*, **97**. 209, 1908 ; F. A. Gooch and J. Howland, *Amer. Journ. Science*, (3), **58**. 375, 1894 ; *Zeit. anorg. Chem.*, **7**. 132, 1894 ; A. Stähler and B. Tesch, *ib.*, **98**. 1, 1916 ; F. W. Clarke, *A Recalculation of the Atomic Weights*, Washington, 386, 1910 ; L. Staudenmaier, *Untersuchungen über das Tellur*, Leipzig, 1895 ; *Zeit. anorg. Chem.*, **10**. 189, 1895 ; K. Seubert, *ib.*, **33**. 247, 1903 ; **35**. 205, 1903 ; P. Köthner, *ib.*, **34**. 402, 1903 ; *Liebig's Ann.*, **319**. 1, 1901 ; *Das reine Tellur und sein Atomgewicht*, Halle, 1901 ; R. Metzner, *Compt. Rend.*, **126**. 1716, 1898 ; *Ann. Chim. Phys.*, (7), **15**. 203, 1898 ; *Sur quelques composés du sélénium et du tellure*, Paris, 1898 ; K. B. Heberlein, *Beiträge zur Kenntniss des Tellurs*, Basel, 1898 ; *Berg. Hütt. Ztg.*, **54**. 41, 1895 ; A. Scott, *Proc. Chem. Soc.*, **18**. 112, 1902 ; O. Steiner, *Ber.*, **34**. 570, 1901 ; G. Pellini, *ib.*, **34**. 3807, 1901 ; *Gazz. Chim. Ital.*, **32**. i, 131, 1902 ; **33**. ii, 35, 1903 ; **34**. i, 132, 1904 ; *Atti Accad. Lincei*, (5), **21**. i, 218, 1912 ; G. Gallo, *ib.*, (5), **14**. i, 23, 104, 1905 ; *Gazz. Chim. Ital.*, **35**. ii, 245, 1905 ; A. Gutbier, *Liebig's Ann.*, **320**. 52, 1902 ; **342**. 266, 1905 ; *Sitzber. Phys. Med. Soc. Erlangen*, **37**. 270, 1908 ; *Studien über das Tellur*, Leipzig, 1901 ; J. F. Norris and H. Fay, *Amer. Chem. Journ.*, **20**. 278, 1898 ; V. Lenher, *Journ. Amer. Chem. Soc.*, **30**. 741, 1908 ; **31**. 20, 1909 ; J. F. Norris, *ib.*, **28**. 1675, 1906 ; L. M. Dennis and R. P. Anderson, *ib.*, **36**. 882, 1914 ; W. L. Dudley and P. C. Bowers, *ib.*, **35**. 875, 1913 ; W. Marckwald, *Ber.*, **40**. 4730, 1907 ; W. Marckwald and A. Foizik, *ib.*, **43**. 1710, 1910 ; P. Bruylants and C. Desmet, *Bull. Soc. Chim. Belg.*, **28**. 264, 1914 ; P. Bruylants and J. Michielsen, *Bull. Acad. Belg.*, (5), **5**. 119, 1919.

[4] H. Wilde, *Compt. Rend.*, **127**. 616, 1898 ; P. Kusnetzoff, *Proc. Polyt. Inst. Novotscherkask*, **1**. ii, 380, 1912 ; G. N. Wyrouboff, *Les actualités chimiques*, **1**. 18, 1896 ; A. Gutbier and F. Flury, *Journ. prakt. Chem.*, (2), **75**. 99, 1905 ; J. W. Retgers, *Zeit. phys. Chem.*, **8**. 72, 1891 ; **9**. 399, 1892 ; **10**. 533, 1892 ; **12**. 598, 1893 ; *Zeit. anorg. Chem.*, **12**. 98, 1896 ; K. Seubert, *ib.*, **33**. 246, 1903 ; W. Muthmann, *Zeit. phys. Chem.*, **8**. 396, 1891 ; *Ber.*, **26**. 1008, 1893 ; A. Werner, *ib.*, **38**. 914, 1905 ; *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*, Braunschweig, 3, 1905 ; London, 3, 1911.

[5] A. van den Broek, *Phys. Zeit.*, **14**. 32, 1913 ; H. G. J. Moseley, *Phil. Mag.*, (6), **26**. 1024, 1913 ; (6), **27**. 703, 1914.

[6] F. W. Aston, *Nature*, **114**. 717, 1924 ; *Phil. Mag.*, (6), **42**. 140, 1921 ; (6), **45**. 242, 1923 ; (6), **49**. 1191, 1925.

[7] N. Bohr, *Nature*, **112**. Suppl., 1923 ; M. L. Huggins, *Journ. Phys. Chem.*, **26**. 601, 1922 ; A. L. Foley, *Proc. Indiana Acad.*, **34**. 185, 1925 ; C. D. Niven, *Phil. Mag.*, (7), **3**. 1314, 1927 ; H. Pettersson and G. Kirsch, *Atomzertrümmerung*, Leipzig, 104, 1926 ; *Sitzber. Akad. Wien*, **134**. 491, 1925 ; C. P. Smyth, *Phil. Mag.*, (6), **50**. 361, 1925 ; H. G. Grimm and A. Sommerfeld, *Zeit. Physik*, **36**. 36, 1926 ; H. Müller, *Sitzber. Akad. Wien*, **135**. 563, 1926 ; G. I. Pokrowsky, *Zeit. Physik*, **57**. 560, 1929 ; J. D. M. Smith, *Journ. Chem. Soc.*, 2029, 1927 ; J. C. Slater, *Phys. Rev.*, (2), **36**. 57, 1930.

§ 6. Hydrogen Telluride

J. W. Ritter[1] observed that when water is electrolyzed with a tellurium cathode, no hydrogen is evolved on the metal, but the liquid is coloured owing, he supposed, to the formation of a tellurium hydride ; H. Davy also found that, under similar circumstances, the water about the cathode acquires a purple tint owing to the formation of hydrogen telluride. If air be present, a brown powder is precipitated which he regarded as a tellurium hydride containing a smaller quantity of hydrogen. On the other hand, H. G. Magnus showed that the brown powder is nothing but metallic tellurium, and it is precipitated even when thoroughly boiled water is employed because of the diffusion of cathodic oxygen into the liquid. If the water be acidified, no brown powder is deposited because the hydrogen telluride which is then produced, being but slightly soluble in the acid liquor, escapes as a gas. Gaseous **hydrogen telluride,** H_2Te, was discovered by H. Davy.

H. Davy observed that when the telluride—obtained by electrolyzing potassium hydroxide by means of a tellurium cathode ; or by heating potassium and tellurium together—is treated with dil. hydrochloric acid, there is a violent effervescence, and an aëriform compound of tellurium and hydrogen is produced which smells very like hydrogen sulphide, and which gives elemental tellurium when it comes in contact with air. As indicated previously, H. Davy, F. Becker, J. Löwe, E. Priwoznik, F. Jones, B. Brauner, A. Ditte, and A. Gutbier discussed the direct union of hydrogen with heated tellurium. M. G. Weber obtained only traces of the telluride to be formed by the direct union of the two elements. E. Pozzi-Escot observed only a very slight hydrogenation of tellurium occurs during diastatic fermentation. Hydrogen telluride is produced by the action of acids on tellurides—*e.g.* H. Davy, and A. Bineau used potassium telluride ; J. J. Berzelius, zinc or iron telluride ; and M. Berthelot and C. Fabre, magnesium telluride. M. G. Weber obtained only a poor yield by the action of an acid on magnesium telluride ; and E. Ernyei, a gas with only 5 per cent. of hydrogen telluride. F. Wöhler, L. M. Dennis and R. P. Anderson, and R. de Forcrand and H. Fonzes-Diacon found that water acting on aluminium telluride furnishes hydrogen telluride ; E. Divers and M. Shimose acted on zinc with a soln. of tellurium dioxide in sulphuric acid. J. C. Poggendorff obtained hydrogen telluride by the electrolysis of dil. sulphuric acid with a tellurium cathode. A. C. Vournasos observed the formation of hydrogen telluride when tellurium is heated with sodium formate to 400°. The yield is limited because of the reverse reaction—the decomposition of the telluride. In all these cases, the product is contaminated with much hydrogen. By the electrolysis of 50 per cent. sulphuric acid, in an apparatus resembling Fig. 6, E. Ernyei obtained a gas containing only 5 to 6 per cent. of hydrogen. M. G. Weber also obtained the best yield by the electrolytic process. E. Ernyei's apparatus is as follows :

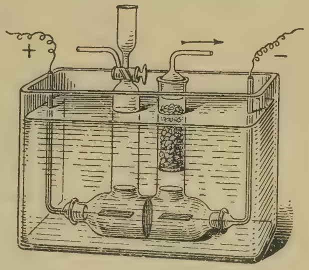


Fig. 6.—The Preparation of Hydrogen Telluride.

> The negative pole is of tellurium ; the electrolyte of 50 per cent. sulphuric acid is cooled during the electrolysis between −15° and −20°. The electrolytic cell has a diaphragm, Fig. 6, of parchment paper to retard movements of the electrolyte. Two glass tubes rise from this cell—the one over the positive pole is fitted with a two-way cork, funnel and bent tube. The latter is to introduce liquid into the cell, and the former is to allow air to be washed from the apparatus by a current of hydrogen before the electrolyte is introduced, and afterwards for the exit of the anode gases. The tube over the negative pole has a partition above which calcium chloride and phosphorus pentoxide can be placed for drying the gas. The fittings are all of glass since cork and rubber decompose the gas. W. Hempel and M. G. Weber cooled the vessel with solid carbon dioxide and alcohol ; and protected the apparatus from light.

L. M. Dennis and R. P. Anderson prepared the gas by the electrolysis of a 50 per cent. soln. of phosphoric acid using a tellurium cathode and platinum anode. The hydrogen telluride was purified by liquefaction, and fractional distillation a number of times. P. Bruylants and J. Michielsen purified the gas from the electrolysis of sulphuric acid in a similar way, and employed it in their determinations of the at. wt. of tellurium. L. Moser and K. Ertl said that the best way of preparing the gas is to drop powdered aluminium telluride into dil. hydrochloric acid in an atm. of nitrogen. The best yield was 80 per cent. of the theoretical. The gas was liquefied in a tube cooled with a mixture of solid carbon dioxide and ether. Liquid hydrogen telluride is sensitive to light, but the dry gas is stable in light. F. Paneth and co-workers observed that hydrogen telluride is formed by an electric discharge with tellurium electrodes in hydrogen.

H. Davy described hydrogen telluride as a colourless gas with a fœtid smell like that of hydrogen sulphide ; and M. Berthelot and C. Fabre said that its odour is different from that of hydrogen sulphide, or selenide, and it slightly resembles that of hydrogen arsenide. Its action on the animal economy is very much less irritating than is that of the selenide. A. Bineau estimated the **vapour density** to be 4·49 (air unity) when the calculated value for H_2Te is 4·48. E. Ernyei determined the vap. density to be 4·49. When the gas is cooled with solid carbon dioxide, it forms lemon-yellow, needle-like crystals with the **melting point** —54° according to E. Ernyei, and —48° according to R. de Forcrand and H. Fonzes-Diacon. The liquid is greenish-yellow, and it has a **specific gravity** of 2·57 at 20°; P. Bruylants gave 2·65 at 0°. E. Rabinowitsch gave 48·9 for the mol. vol. H. Remy discussed the structure of hydrogen telluride. P. Bruylants found the **vapour pressure,** *p* mm., to be

	−60°	−50°	−40°	−30°	−20°	−10°	0°
p . .	36	79	139	234	370	555	808

The **boiling point** is 0° at 760 mm. E. Ernyei said the b.p. is over 0°; E. Q. Adams studied the relation between the b.p. and composition. P. Bruylants gave —1·8°, and he estimated the **critical temperature** to be at about 200°. The **triple point** is at —45·4° and 102 mm.; the latent **heat of vaporization** was estimated to be 5·7 cals. M. Berthelot and C. Fabre found that the **heat of formation** is $(H_{2gas}, Te_{cryst.})=H_2Te_{gas}-35{\cdot}0$ Cals.; and R. de Forcrand gave —50·8 Cals. for the solid telluride. The heat of formation of water, hydrogen sulphide and hydrogen selenide are respectively 59·0, 4·6, and —12·3 Cals.; thus showing that in the oxygen group, as in the chlorine group, the energy of combination with hydrogen diminishes as the at. wt. of the element rises. A 0·1*N*-soln. of hydrogen telluride, in the absence of air, according to L. Bruner, has a sp. **electrical conductivity** of 2×10^{-3}, and at this conc. is 50 per cent. ionized. M. de Hlasko found for the mol. conductivity μ, of soln. of hydrogen telluride at 18°; the sp. conductivity k ohms; the **ionization constant** k, where $k=\alpha^2/(1-\alpha)v$; and α represents the **degree of ionization :**

	0·093*N*-	0·0667*N*-	0·06173*N*-	0·3442*N*-	0·02326*N*-	0·01186*N*-	
μ .	56	63	67	855	107·5	136	208·5
k .	0·00124	0·004215	0·004061	0·002942	0·002497	0·001607	0·000579
K .	0·00240	0·00223	0·00226	0·00222	0·00259	0·00250	0·00180
α .	0·148	0·166	0·176	0·225	0·283	0·360	0·549

The mean value of the ionization constant is $K=0{\cdot}00227$ at 18°. Hydrogen telluride thus appears to be a stronger acid than hydrogen fluoride. The increase in the strength of the hydrogen acids of this family of elements thus increases rapidly with increasing at. wt. Thus, the ionization constants for H_2O is $0{\cdot}64\times10^{-14}$, for H_2S, $0{\cdot}91\times10^{-7}$; H_2Se, $1{\cdot}88\times10^{-4}$; and for H_2Te, $2{\cdot}27\times10^{-3}$. The increasing acidity with increasing at. wt. was also noted by L. Bruner

Hydrogen telluride was found by M. Berthelot and C. Fabre to be very unstable even in darkness. E. Ernyei also found that decomposition occurs in a sealed tube, and it can be kept for a couple of days while cooled by a freezing mixture, but even under 0°, it decomposes into tellurium and hydrogen. A. Ditte said that when warmed, it behaves like hydrogen selenide, but at a much lower temp. He said that it becomes more stable at a somewhat higher temp., but at a still higher temp., a large proportion is decomposed. Both H. Davy, and E. Ernyei found that the gas burns in **air** with a pale blue flame forming water, and tellurium dioxide. According to M. Berthelot and C. Fabre, and R. de Forcrand and H. Fonzes-Diacon the gas is decomposed at once by moist air, and a piece of moist filter-paper in contact with the gas is blackened immediately. The gas dissolves in **water** forming a red soln.—presumably owing to the separation of tellurium. The aq. soln. reddens litmus; water with air in soln. at once decomposes the gas. L. Bruner added that if a bubble of oxygen be allowed to come in contact with the aq. soln. of the gas, the soln. is decomposed, tellurium separates, and the conductivity falls to zero, thus proving that the electrical conductivity of the aq. soln. is really due to the hydrogen telluride. H. Davy found that **chlorine** reacts vigorously with the gas forming tellurium which is quickly converted into chloride; and E. Ernyei observed that an aq. soln. of **bromine** is decolorized by the gas; and similarly also with **iodine.** According to C. Whitehead, **tellurium tetrachloride** reacts with the gas: $2H_2Te+TeCl_4=3Te+4HCl$. C. Whitehead said that the soln. in 95 per cent. **alcohol** is stable in air. A. Bineau observed that when heated with **tin,** all the tellurium is withdrawn, and an equal vol. of hydrogen is produced. Hydrogen telluride was found by H. Davy, and J. J. Berzelius to dissolve in an aq. soln. of **alkali hydroxide.** E. Ernyei added that the soln. with alkali hydroxide are colourless, and they become red on exposure to air; if the soln. contains oxygen, tellurium separates, and this subsequently dissolves forming a red soln. of potassium telluride. Hydrogen telluride reduces **ferric chloride** to ferrous chloride; M. Berthelot and C. Fabre represented the reaction $2FeCl_{3aq.}+H_2Te=Te+2FeCl_{2aq.}+2HCl_{aq.}+58{\cdot}24$ Cals. E. Ernyei also found that the gas reduces **mercuric chloride** to mercurous chloride. A. Brukl studied the action of the gas on metal salt soln.—*vide* the tellurides.

According to E. Divers and M. Shimose, if hydrogen telluride made by the action of zinc and sulphuric acid holding tellurium dioxide in soln. be passed into more of the tellurated sulphuric acid, not diluted with water, a red soln. of tellurium sulphotrioxide is formed: $2H_2Te+TeO_2+3H_2SO_4=5H_2O+3TeSO_3$, and as the passage of the gas continues, the red sulphotrioxide is destroyed, and there is formed a brown insoluble substance which in some parts appears in the form of scaly, black particles with a metallic lustre, and which is thought to be **hydrogen pertelluride.** Its solubility in sulphuric acid, and its appearance is said to indicate that it is not elemental tellurium. It may, however, form a red soln. if treated with sulphuric acid containing tellurium sulphate, or if fresh sulphuric acid be added to the mother-liquor. In this case, the sulphuric acid probably exercises an oxidizing power by containing traces of dissolved oxygen, or oxidizing agents. It redissolves in its own mother-liquor when the mixture is exposed to the air, the dissolution proceeding from the surface of the liquid downwards, evidently a case of atm. oxidation. But it also redissolves slowly when sealed up with its mother-liquor in glass tubes in an atm. of hydrogen, and this dissolution of it is accompanied by reduction of the sulphuric acid; for on opening the tubes, the smell of sulphur dioxide is distinct. This reduction of sulphuric acid further shows that the precipitate is not tellurium, as this substance dissolves without forming sulphur dioxide. The hydrogen of the pertelluride is readily oxidized by air in the presence of sulphuric acid, and more slowly by sulphuric acid alone, with the production of sulphur dioxide.

References.

[1] J. W. Ritter, *Denks. München Akad.*, 210, 1808; *Gehlen's Journ.*, **6**. 568, 1808; *Gilbert's Ann.*, **29**. 148, 1808; H. Davy, *Phil. Trans.*, **100**. 161, 27, 1810; H. G. Magnus, *Dissertatio de tellurio*, Berolensis, 1827; *Pogg. Ann.*, **17**. 521, 1829; F. Wöhler, *ib.*, **11**. 161, 1827; J. C. Poggendorff, *ib.*, **75**. 350, 1848; E. Divers and M. Shimose, *Journ. Chem. Soc.*, **43**. 329, 1883; P. Bruylants, *Bull. Acad. Belg.*, (5), **6**. 472, 1920; A. Brukl, *Monatsh.*, **45**. 471, 1924; A. Bineau, *Ann. Chim. Phys.*, (2), **68**. 424, 1838; M. Berthelot and C. Fabre, (6), **14**. 103, 1887; R. de Forcrand and H. Fonzes-Diacon, *ib.*, (7), **26**. 258, 1902; *Compt. Rend.*, **134**. 1209, 1902; A. Ditte, *ib.*, **74**. 984, 1872; E. Ernyei, *Zeit. anorg. Chem.*, **25**. 313, 1900; A. Gutbier, *ib.*, **32**. 31, 1902; L. Moser and K. Ertl, *ib.*, **118**. 269, 1921; C. Whitehead, *Journ. Amer. Chem. Soc.*, **17**. 849, 1895; L. M. Dennis and R. P. Anderson, *ib.*, **36**. 882, 1914; E. Q. Adams, *ib.*, **48**. 870, 1926; A. C. Vournasos, *Ber.*, **43**. 2272, 1910; E. Rabinowitsch, *ib.*, **58**. B, 2790, 1925; J. J. Berzelius, *Schweigger's Journ.*, **6**. 311, 1812; **34**. 78, 1823; *Pogg. Ann.*, **28**. 392, 1833; **32**. 1, 577, 1834; F. Paneth, M. Matthies, and E. Schmidt-Hebbel, *Ber.*, **55**. 775, 1922; M. G. Weber, *Kritsche Studien über die Darstellungsweisen von Selen- und Tellurwasserstoff*, Weida i. Th., 1910; W. Hempel and M. G. Weber, *Zeit. anorg. Chem.*, **77**. 48, 1912; J. Löwe, *Sitzber. Akad. Wien*, **10**. 727, 1853; *Journ. prakt. Chem.*, (1), **60**. 162, 1853; E. Priwoznik, *Vorkommen von Tellur und Gewinnung aus seinen Erzen*, Wien, 1893; *Oesterr. Zeit. Berg. Hütt.*, **45**. 219, 1895; B. Brauner, *Journ. Chem. Soc.*, **55**. 382, 1889; **67**. 527, 549, 1895; *Sitzber. Akad. Wien*, **98**. 456, 1889: *Monatsh.*, **10**. 413, 1889; **12**. 34, 1891; F. Becker, *Liebig's Ann.*, **180**. 259, 1876; E. Pozzi-Escot, *Bull. Soc. Chim.*, (3), **27**. 346, 1902; F. Jones, *Mem. Manchester Lit. Phil. Soc.*, **48**. 16, 1904; M. de Hlasko, *Journ. Chim. Phys.*, **20**. 167, 1923; *Bull. Acad. Polonaise*, 73, 1919; L. Bruner, *Zeit. Elektrochem.*, **19**. 861, 1913; P. Bruylants and J. Michielsen, *Bull. Acad. Belg.*, (5), **5**. 119, 1919; R. de Forcrand, *Journ. Chim. Phys.*, **15**. 517, 1917; H. Remy, *Zeit. anorg. Chem.*, **116**. 255, 1921.

§ 7. The Tellurides

A. F. Hallimond [1] discussed the isomorphism of the sulphides, selenides, and tellurides. A. Bineau obtained colourless plates of **ammonium hydrotelluride,** $(NH_4)_2HTe$, by bringing ammonia in contact with an excess of hydrogen telluride. E. Wendehorst obtained the colourless salt by passing purified hydrogen selenide into a sat. soln. of ammonia in an atm. of nitrogen, and cooled below 30°.

H. Davy [2] prepared **potassium telluride,** presumably K_2Te, by warming a mixture of the two elements in an atm. of hydrogen; combination occurs with incandescence. C. A. Tibbals also obtained potassium telluride by the direct union of the elements. H. Davy obtained this compound by the electrolysis of molten potassium hydroxide, using tellurium electrodes; if a conc. soln. of potassium hydroxide is similarly treated, the tellurium dissolves forming a red soln. which is rapidly decomposed with the precipitation of tellurium by the oxygen liberated at the anode. J. J. Berzelius, and G. Magnus melted tellurium with potassium hydroxide or carbonate, and boiled tellurium with conc. potash-lye; in both cases some potassium tellurite is formed; but not so if zinc be present since F. and C. Heberlein observed that by boiling oxy-salts of tellurium with conc. potash-lye, and granulated zinc, the liquid becomes red owing to the formation of potassium telluride. This reaction is recommended as a test for tellurium in minerals. J. J. Berzelius, M. Berthelot and C. Fabre, and E. Ernyei obtained potassium telluride by the action of hydrogen telluride on a soln. of potassium hydroxide in the absence of air; A. Oppenheim, by melting tellurium with potassium cyanide; H. Davy, by heating the tellurite or tellurate with carbon, or, according to A. Oppenheim, in hydrogen; and C. Hugot, by the action of a soln. of potassium in liquid ammonia on an excess of tellurium.

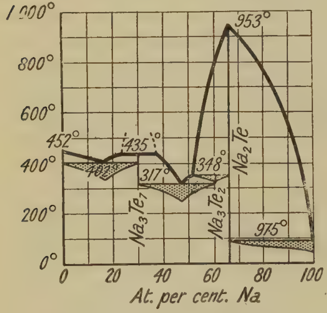


FIG. 7.—Equilibrium Diagram of the System: Na–Te.

M. Berthelot and C. Fabre described their preparation as colourless crystals; E. Demarçay said that the soln. is pale yellow; C. Hugot's preparation was amorphous and white; H. Davy's preparations were copper-red, or steel-grey. M. Berthelot and C. Fabre said that potassium telluride forms a colourless soln. with oxygen-free water. The coloured preparations dissolve in water forming a red liquid. The colour may be due to the presence of a polytelluride, of the monoxide, or of colloidal tellurium. If the strongly alkaline soln. be treated with a reducing agent—say, phosphorus, a hypophosphite, or aluminium—E. Demarçay found that the soln. becomes pale yellow; and similarly, if a soln. of potassium tellurite be treated with a reducing agent, it becomes violet and then yellow. According to M. Berthelot and C. Fabre, and E. Demarçay, the colourless soln. rapidly reddens in contact with air, and, added H. Davy, the red soln. becomes colourless owing to the deposition of the separated tellurium. J. J. Berzelius said that soln. of tellurium in conc. alkali-soln. are decomposed by acids with the evolution of hydrogen telluride. C. A. Tibbals said that the telluride is precipitated in crystals by adding alcohol to a conc. soln. A. Brinkmann did not obtain **lithium telluride** by boiling tellurium with a conc. soln. of lithium hydroxide, or by melting tellurium with lithium hydroxide. G. Pellini and E. Quercigh investigated the sodium tellurides by thermal methods, and the results, summarized in Fig. 7, show that only these compounds which melt unchanged can exist under these conditions, namely, the normal telluride. It is white, and deliquescent; and rapidly darkens on exposure to air. There is also **sodium tritaditelluride,** Na_3Te_2, with a grey metallic appearance; and **sodium tritaheptatelluride,** Na_3Te_7. Neither Na_4Te_3 nor Na_2Te_3 were obtained. H. Davy obtained **sodium telluride,** Na_2Te, by the methods employed for potassium telluride ; likewise also A. Oppenheim, E. Ernyei, and C. A. Tibbals. According to L. A. Tschugaeff and V. G. Chlopin, when tellurium is heated with an alkaline soln. of sodium hyposulphite in the absence of air, tellurium is converted into the unstable sodium telluride, Na_2Te, and sodium sulphide is formed at the same time. The tellurium is probably first transformed by the sodium hydroxide into a mixture of sodium tellurite and telluride, the latter being then converted by the tellurium into polytellurides, which undergo reduction by the sodium hyposulphite: $Na_2S_2O_4+Na_2Te_2+4NaOH=2Na_2SO_3+2Na_2Te+2H_2O$. This reduction is analogous to the action of the hyposulphite on sodium polysulphides. It is possible that the tellurium combines with the sulphoxylate part of the hyposulphite mol., $Na.SO.ONa+Te=Na.Te.SO.ONa$, the unstable compound thus obtained reacting with the sodium hydroxide, thus: $Na.Te.SO.ONa+2NaOH=Na_2Te+O.S(ONa)_2+H_2O$. The formation of the sodium sulphide also obtained in the reaction is probably explained by the equations: $2Na_2S_2O_4+2NaOH=Na_2S_2O_3+2Na_2SO_3+H_2O$, and $Na_2S_2O_3+Na_2S_2O_4+4NaOH=Na_2S+3Na_2SO_3+2H_2O$. The extreme instability of sodium hyposulphite makes it difficult to prepare sodium telluride in large quantities in the above manner. A good yield may, however, be obtained by heating, in a current of hydrogen, a mixture of a gram of tellurium, 6 grms. of sodium formaldehyde-sulphoxylate (rongalite), and 40 c.c. of a 10 per cent. sodium hydroxide soln.: $HO.CH_2.O.SONa+Te+3NaOH=CH_2O+Na_2Te+Na_2SO_3+H_2O$. Sodium telluride is instantaneously decomposed in the air, with separation of tellurium. D. M. Liddell said that if kept from air, sodium telluride is the colour of potassium permanganate, but in air it is decomposed setting free tellurium with the formation of potassium hydroxide. Contrary to G. Pellini and E. Quercigh, C. A. Kraus and S. W. Glass find that sodium telluride and tellurium are miscible in all proportions. The equilibrium diagram is shown in Fig. 8. In addition to the normal telluride, Na_2Te, there are formed the ditelluride with a transition point at 355°, and the hexatelluride with a congruent m.p. at 436°. There are eutectics at 319° with 43 at. per cent. of Na, and at 402·5° with 12·5 at. per cent. Na.

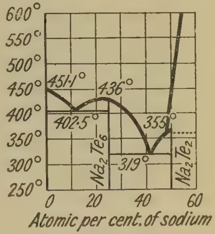


Fig. 8.—The Equilibrium Diagram of Sodium Telluride and Tellurium.

According to C. A. Kraus and C. Y. Chiu, the initial compound formed in the reaction between sodium and tellurium in liquid ammonia is the normal telluride, Na_2Te, which is in equilibrium with **sodium ditelluride,** Na_2Te_2. Figs. 7 and 8 show the range of stability of the compound. C. A. Kraus and S. W. Glass found that it has a transition point at 355°. Its electrical resistance is given in Figs. 9 and 10. The soln. in equilibrium with free tellurium has a composition which varies as a function of the concentration, and the maximum conc. of tellurium corresponds with **sodium tetratelluride,** Na_2Te_4. C. A. Kraus and E. H. Zeitfuchs discussed the mol. wt. of the sodium-tellurium complex formed in liquid ammonia. Tellurides of the heavy metals are formed by double decomposition between sodium telluride and aq. soln. of salts of the heavy metals. C. A. Kraus and S. W. Glass observed the formation of **sodium hexatelluride,** Na_2Te_6, and its equilibrium conditions are illustrated in Fig. 8. It melts at 436° ; and its electrical resistance is indicated in Figs. 9 and 10. C. A. Tibbals said that sodium telluride forms small colourless crystals with much water of crystallization ; and that tellurium dissolves in an aq. soln. of this salt forming **sodium tetritatritelluride,** Na_4Te_3. Tellurium does not dissolve in a soln. of sodium telluride beyond the proportion 4 : 3, and when this soln. is concentrated by evaporation, it breaks down into the normal telluride and tellurium. According to C. Hugot, **sodium hemitritelluride,** Na_2Te_3, is produced by the action of a soln. of sodium in liquid ammonia on an excess of tellurium ; and similarly also with **potassium hemitritelluride,** K_2Te_3. The latter furnishes a violet liquid which becomes brown and viscid at −25°, and when stirred, freezes to a solid. This melts at −15°, and as the ammonia evaporates, at ordinary temp., there remains the hemitritelluride as a dark brown crystalline mass; which, under press. absorbs ammonia and becomes liquid. L. A. Tschugaeff and V. G. Chlopin observed that a soln. of sodium telluride reacts with benzyl chloride or phenylbenzyldimethylammonium chloride forming *benzyl telluride*, $Te(C_6H_5.CH_2)_2$.

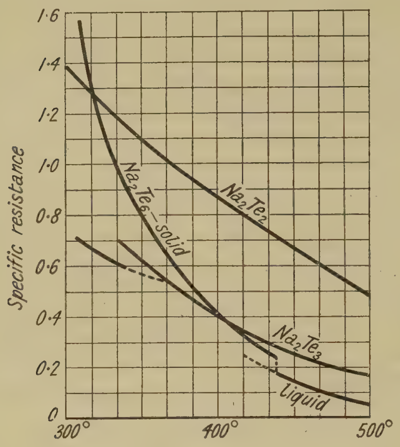


FIG. 9.—The Resistance of the Sodium Tellurides.

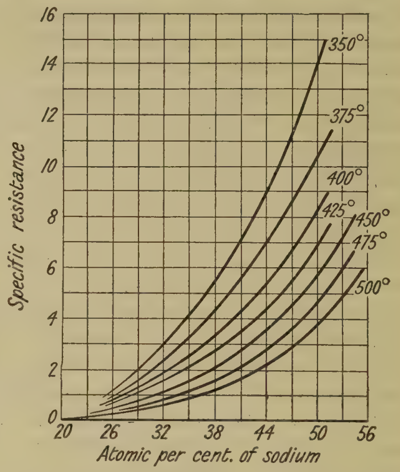


FIG. 10.—The Resistance of the Sodium Tellurides.

J. J. Berzelius[3] prepared a pale red alloy by melting together copper and tellurium; M. Chikashige obtained the alloys by melting mixtures of the two elements in a current of carbon dioxide. T. Parkman said that tellurium precipitates a little copper from cold soln. of copper sulphate or acetate, and likewise also with boiling soln. After boiling tellurium for 4 or 5 hrs. with a soln. of copper acetate, a black powder with the composition of *copper hemitritelluride*, Cu_2Te_3, was formed; and with a boiling soln. of copper sulphate a black powder with the composition of *copper telluride*, CuTe. C. A. Tibbals obtained the monotelluride and also the hemitritelluride by treating a soln. of a copper salt respectively with normal sodium telluride, Na_2Te, and the tetritatritelluride, Na_4Te_3. F. Garelli obtained what appeared to be mixtures of copper tetritatelluride and monotelluride by wrapping a piece of tellurium with copper wire and immersing it in a soln. of copper sulphate. A. Brukl obtained cuprous telluride by the action of sodium telluride on a soln. of sodium cuprous chloride. B. Brauner and B. Kuzma found that in precipitating tellurium by sulphur dioxide from soln. of salts of other metals like copper, some of the metal is precipitated with the tellurium, and this the more the longer the action and the more conc. the soln. W. E. Ford reported a massive mineral which he called **richardite**—after T. A. Richard—occurring in the Good Hope Mine, Vulcan, Colorado. Its composition corresponds with *cuprous telluride*, Cu_4Te_3, or $Cu_2Te.2CuTe$. It has a rich purple colour; sp. gr. 7·54; and hardness 3·5. N. A. Puschin said that this product is a solid soln. of telluride and hemitelluride. E. T. Wherry found richardite to be a poor radiodetector. W. M. Davy and C. M. Farnham observed the behaviour of polished surfaces of the mineral towards etching agents.

According to M. Chikashige, the f.p. curve of the copper-tellurium alloys, Fig. 11, shows a eutectic point at 344° and 17·3 per cent. of copper, and there is a break at 620° with about 34 per cent. of copper; and one at 855°, with 50 per cent. of copper. The break with 50 per cent. of copper corresponds with **copper hemitelluride,** Cu_2Te, which is miscible with copper only to a limited extent—at about 1030°, the hemitelluride dissolves 1 to 2 per cent. of copper, and copper about 4 per cent. of tellurium. From 32·7 to 50 per cent. of copper, the hemitelluride crystallizes primarily in solid soln. with tellurium; and at 623° the mixed crystals with 45 per cent. of copper react with the fused mass to form **copper tetritatritelluride,** Cu_4Te_3, analogous in composition with richardite. A. Mazzucchelli and A. Vercillo obtained a substance of this composition by the action of copper on tellurium tetrachloride, but they regarded it as a mixture of TeCu and $TeCu_2$. According to M. Chikashige, the tetritatritelluride has a transition point at 365° marked by a considerable development of heat. B. Brauner prepared the monotelluride by passing the vapour of tellurium in a current of carbon dioxide over heated copper; and J. Margottet, by heating a mixture of tellurium and copper to redness in an atm. of nitrogen. M. L. Huggins studied the atomic structure. G. von Hevesy and W. Serth studied the diffusion of silver telluride in copper telluride. M. Chikashige found that the hemitelluride has two transition points at 387° and 351°, and the latter is lowered to 334° by the addition of 5 per cent. of tellurium. A. Beutall obtained hair-copper by heating the telluride in a sealed tube at 350°–600°. C. Fabre gave 7·15 Cals. for the heat of formation, and added that the alloy is not stable in air. B. Brauner added that the crystals are rhombohedral, and when heated for a long time they are decomposed with the separation of copper. W. P. Crawford described a massive, bluish-black mineral in the tellurium deposits of Colorado. He called it **weissite**—after L. Weiss; its composition corresponds with **copper pentitatritelluride,** Cu_5Te_3. Its sp. gr. is about 6, and its hardness 3. It gives a violet colour with warm, conc. sulphuric acid. The *weissite* of W. P. Crawford is probably richardite.

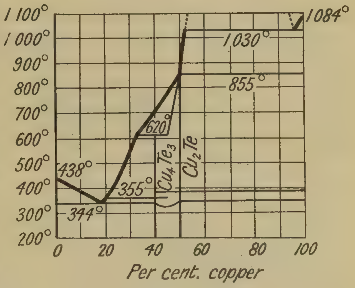


FIG. 11.—Freezing-point Curve of Copper-Tellurium Alloys.

According to N. A. Puschin, the alloys rich in copper are dark grey, brittle, and crystalline; those with 30 to 33 at. per cent. of tellurium are much darker, and more brittle; the colour then becomes dark violet with about 40 at. per cent. of tellurium; the colour becomes paler as the proportion of tellurium rises to 50 at. per cent., when the colour becomes yellow; with higher proportions of tellurium the colour becomes grey. W. C. Roberts-Austin found that the addition of tellurium reduces the malleability of copper. M. Chikashige said that the re-melting of the alloy does not remove the copper; but P. Köthner found that all the tellurium can be removed by distillation in vacuo. I. Stransky discussed the rectifying action of the heavy metal tellurides; and G. P. Thomson, electron diffraction rings. N. A. Puschin found that the potential of copper in the cell Cu | N-$CuSO_4$ | $CuTe_n$ shows breaks corresponding with Cu_2Te, and CuTe, Fig. 12. According to B. Brauner, the tellurium is not removed by fusion with sulphur and sodium carbonate; or, according to M. Chikashige, by fusion with cuprous oxide. F. W. Hinrichsen and O. Bauer said that the telluride dissolves in a soln. of potassium cyanide forming a polytelluride; and when shaken in air, the reddish-violet soln. becomes colourless owing to the deposition of the tellurium in grey flakes. E. Heyn and O. Bauer found that the soln. in potassium cyanide gives a dark grey precipitate with alcohol and cadmium acetate; and C. Whitehead obtained tellurium by electrolyzing the soln. G. Tammann studied the chemical activity of the alloys.

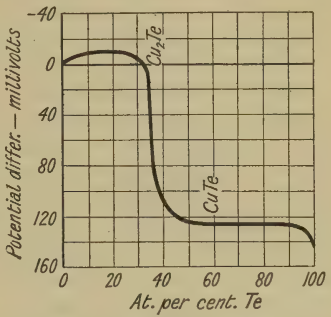


FIG. 12.—Potential Differences of Cu | N-$CuSO_4$ | $CuTe_n$.

The silver tellurides are represented in nature by the three minerals stützite, Ag_4Te; hessite, Ag_2Te; and empressite, AgTe. The mineral **stützite,** probably from Nagyag, Transylvania, was shown by A. Schrauf[4] to have a composition approximating **silver tetritatelluride,** Ag_4Te; and it was named after A. Stütz, who, in 1803, described what appears to have been the same mineral. It is leaden grey, with a reddish tinge. V. Goldschmidt, and C. Hintze regard it as hexagonal or pseudohexagonal with the axial ratio $a:c=1:1{\cdot}2530$; or, as A. Schrauf prefers to regard it, monoclinic with the axial ratios $a:b:c=1{\cdot}73205:1:1{\cdot}24829$, and $\beta=89° 33'$. E. S. Dana emphasized the resemblance to dyscrasite, and chalcocite and said that like them, it may be rhombic. A. des Cloizeaux also regarded stützite as having rhombic symmetry. There is no evidence of the existence of a tetritatelluride on the f.p. curve, Fig. 13. The f.p. curve was first explored, in a preliminary way, by H. Pélabon,[5] who found two eutectics—one at 345° and 34 at. per cent. of silver, and the other at 825° with 78 per cent. of silver—and a maximum representing the normal telluride at 965°. G. Pellini and E. Quercigh made a more detailed study, and their work as revised by M. Chikashige and I. Saito, is illustrated by Fig. 13. Two compounds are indicated on the curve; the normal telluride melting sharply at 957°; and the other **silver heptitatetratelluride,** Ag_7Te_4. The heptitatetratelluride decomposes below its m.p., and exists in two modifications, each of which corresponds with a short branch of the f.p. curve. β-Ag_7Te_4 is formed from Ag_2Te and liquid at 443°; and changes into the α-modification at 403°. Solid soln. are not formed. Eutectics occur at 32 per cent. Ag and 350° and at 87·5 per cent. Ag and 870°, respectively. Annealing experiments indicate that the transformation is one of a single compound, and that a second compound, such as Ag_3Te_2, is not formed. In Fig. 13, the area *A* represents Te+melt; *B*, Te+eutectic E_1; *C*, α-Ag_7Te_4+eutectic E_1; *D*, α-Ag_7Te_4+melt; *E*, β-Ag_7Te_4+melt; *F*, β-Ag_7Te_4+Ag_2Te; *G*, Ag_2Te+melt; *H*, α-Ag_7Te_4+Ag_2Te; *I*, Ag_2Te+melt; *J*, Ag_2Te+eutectic E_2; *K*, Ag+eutectic E_2; *L*, Ag+melt.

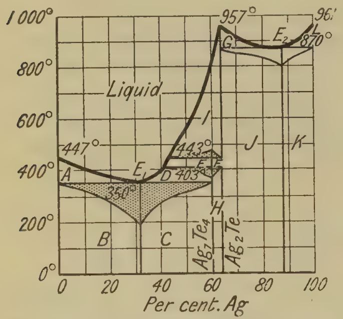


FIG. 13.—Freezing-point Curve of the System: Ag–Te.

The compound which M. Chikashige and I. Saito regarded as hepitatetratelluride was considered by G. Pellini and E. Quercigh to be **silver monotelluride,** AgTe, and they said that its existence is marked by a break in the curve at 444°; and that it undergoes a polymorphic change at 412°. The monotelluride is represented in nature by the mineral **empressite** obtained by W. M. Bradley from the Empress Josephine Mine, Kerber Creek District, Colorado. It occurs in granular and compact masses with a fine conchoidal or uneven fracture, and a pale bronze colour. It is readily soluble in nitric acid. Its hardness is 3·0 to 3·5. E. T. Wherry found empressite to be a poor radio-detector. The mineral was also analyzed by E. J. Dittus; and W. T. Schaller considered it to be a kind of gold-free muthmannite—*vide infra.*

G. Rose[6] described a mineral occurring in the Savodinsky Mine, Zyrianovsky, Altai, Siberia, which he designated *Tellursilber;* J. J. N. Huot, and W. Haidinger called it *savodinskite,* in allusion to its origin; and J. Fröbel, **hessite**—after H. Hess. The term hessite is commonly employed although it has not first claim. A. Schrauf supposed the mineral from Rezbanya, Hungary, to be isomorphous with silver glance and therefore called it *Tellursilberglanz,* and reserved the term *Tellursilberblende* for stützite. Analyses of the mineral have been reported by G. Rose, S. Koch, W. Petz, K. A. Nemadkevich, G. A. Kenngott, F. J. Malaguti and J. Durocher, F. Becke, J. Loczka, C. F. Rammelsberg, G. Küstel, F. A. Genth, F. A. Genth and S. L. Penfield, I. Domeyko, A. des Cloizeaux, F. W. Clarke, A. Carnot, T. L. Walker and A. L. Parsons, E. V. Shannon, and E. S. Simpson. The results agree that hessite is normal silver telluride, *i.e.* **silver hemitelluride,** Ag_2Te, in which gold often replaces part of the silver until the hessite merges into petzite. The occurrence of the mineral in Zyrianovsky, Altai, Siberia, was described by G. Rose, N. von Kokscharoff, and P. von Jeremejeff; in Nagyag, Zalathna, Botes, etc., Transylvania, by P. Groth, G. vom Rath, A. Schrauf, J. A. Krenner, G. A. Kenngott, and F. Becke; in Rezbanya, Hungary, by C. F. Rammelsberg, K. F. Peters, A. Schrauf, and F. von Richthofen; in Kara Issar, Asia Minor, by A. des Cloizeaux; in Karangahake, New Zealand, by J. D. Dana; Kalgoorlie, West Australia, by E. S. Simpson; in Coquimbo, Chili, by I. Domeyko; in Refugio and Quiteria, Mexico, by C. F. de Landero, and F. W. Clarke; in California, Colorado, and Utah, United States, by B. Silliman, W. P. Blake, G. J. Brush, G. Küstel, H. J. Burkart, F. A. Genth, and F. A. Genth and S. L. Penfield.

B. Brauner prepared this telluride by passing the vapour of tellurium over silver at a red-heat. J. Margottet obtained regular octahedra by passing the vapour of tellurium in a current of nitrogen over silver at a dull red-heat. G. Rose, and B. Brauner prepared it by heating a mixture of the two elements. H. Pélabon, G. Pellini and E. Quercigh, and M. Chikashige and I. Saito also obtained it by the direct union of the elements. The conditions of equilibrium are illustrated in Fig. 7. R. D. Hall and V. Lenher obtained this telluride by passing hydrogen telluride into an ammoniacal soln. of silver nitrate, but the black precipitate always contains an excess of silver. C. A. Tibbals, and A. Brukl obtained this telluride as a dark brown or black flocculent precipitate by the action of a soln. of sodium telluride on a soln. of silver acetate in acetic acid; and J. B. Senderens, by the action of tellurium on a soln. of silver nitrate at 100°: $4AgNO_3+3Te+3H_2O=2Ag_2Te+H_2TeO_3+4HNO_3$; the reaction is slow at ordinary temp.—R. D. Hall and V. Lenher represented the reaction $4AgNO_3+3Te=2Ag_2Te+Te(NO_3)_4$. B. Brauner, and R. D. Hall and V. Lenher obtained a product resembling the mineral by passing carbon monoxide or ammonia over silver tellurite heated to a high temp.

The mineral occurs in compact or fine-grained masses—rarely coarse grained. The colour is lead-grey, steel-grey, or iron-black. E. F. Glocker called the yellow earthy telluride *müllerin*, or *Nagyager silver*. The mineral also occurs in crystals more or less modified and often much distorted. According to A. Schrauf, P. Groth, H. Rose, T. L. Walker and A. L. Parsons, J. A. Krenner, C. Palache, V. Rosicky, R. Pilz, and L. Tokody, they are cubic. The distortion led H. Hess, and G. Suckow to assume that the crystals are rhombohedral; G. A. Kenngott, and K. F. Peters, rhombic; and F. Becke, triclinic. According to L. S. Ramsdell, the X-radiogram of hessite indicates that the mineral is pseudo-cubic and probably rhombic. The cubic form is said to represent a high temp. modification. The artificial crystals prepared by J. Margottet were regular octahedra. The cleavage of hessite is indistinct. M. L. Huggins studied the atomic structure of the crystals; and T. Andrews, J. Arnold and J. Jefferson, F. Osmond and W. C. Roberts-Austen, the structure of the alloys. F. A. Genth gave 8·359 for the sp. gr. of varieties free from gold, while G. Rose gave 8·412–8·565. These numbers are probably too high. F. J. Malaguti and J. Durocher, and G. A. Kenngott gave 8·071. W. Petz gave 8·31 to 8·45 for specimens with 0·69 per cent. of gold; F. A. Genth, 8·178. G. Küstel gave 9·0 to 9·4 for a sample with 24·80 per cent. of gold. F. Henglein gave 41·3 for the mol. vol. G. Pellini and E. Quercigh said that the silver tellurium alloys are crystalline, and have a metallic appearance, changing from grey to white as the proportion of silver increases. The brittleness diminishes from tellurium to silver. W. C. Roberts-Austen studied the mechanical properties of these alloys. The hardness of hessite is about 2·5. L. Jordan and co-workers measured the hardness, tensile strength, and elongation of silver-tellurium alloys. G. von Hevesy and W. Serth studied the diffusion of silver in silver ditelluride, and of silver telluride in copper telluride. H. Pélabon gave 955° for the m.p.; G. Pellini and E. Quercigh, 959°; and M. Chikashige and I. Saito, 957°—*vide* Fig. 13.

J. Margottet found that the mineral is partially decomposed at a white-heat; and J. Joly, that hessite sublimes at about 900°. K. Friedrich and A. Leroux said that, unlike silver sulphide, the telluride is not altered by light; and H. E. McKinstry found no effect was produced by exposing the mineral to the electric arc-light. A. Beutell obtained hair-silver by heating the telluride in a heated tube at 350°–600°. A. de Gramont studied the spark spectrum of the mineral. F. Beijerinck described the mineral as an electric conductor. T. W. Case said that the electrical resistance is less than one megohm; and that the conductivity is not affected by exposure to light. R. G. Harvey studied the subject. N. A. Puschin's observations on the potential difference in the cell Ag | $\frac{1}{7}N$-AgNO$_3$ | AgTe$_n$(millivolts) show the existence of only one telluride, Ag$_2$Te. E. T. Wherry called hessite a fair radio-detector. J. M. Rivière's measurements of alloys with 2 (continuous curves) and with 20 (dotted curves) per cent. of silver are summarized. The different curves represent specimens which have been previously heated and at first rapidly cooled to the temp. indicated and then slowly cooled. Below 200°, the resistance is a function of two variables (i) the temp. of measurement; and (ii) the temp. of annealing. For the 12–30 per cent. alloys there is a discontinuity at —20°; and for nearly pure tellurium, one at 415°. J. Margottet observed that when heated to near the m.p. of silver telluride in a current of hydrogen, hair-silver is produced. J. Joly observed that a sublimate is formed between 820° and 930°. C. A. Tibbals observed that the precipitated telluride is quite stable in air, even when moist, and is not acted on by acids other than nitric acid. Hessite also dissolves in hot nitric acid; and when the mineral is heated with conc. sulphuric acid it forms a red or purple liquid which becomes clear when diluted with water, and tellurium is precipitated. W. M. Davy and C. M. Farnham studied the etching of polished surfaces of hessite. R. D. Hall and V. Lenher said that sulphur monochloride converts it into tellurium tetrachloride, etc. G. Tammann studied the chemical activity of the alloys.

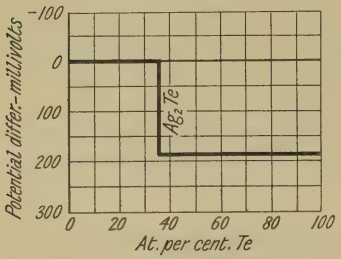


FIG. 14.—Potential Difference of Ag | $\frac{1}{7}N$-AgNO$_3$ | AgTe$_n$.

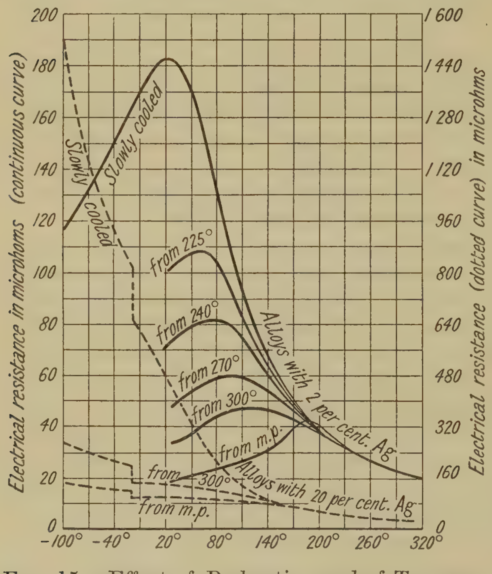


FIG. 15.—Effect of Preheating and of Temperature on the Electrical Resistance of Tellurium-Silver Alloys.

J. A. Krenner,[7] and G. vom Rath described, about the same time, a *krystallisierte Tellurgoldverbindung* from Nagyag, Transylvania. A yellow earth from Nagyag, Transylvania, described by M. H. Klaproth, A. Stütz, W. Phillips, W. Haidinger, and W. H. Miller was probably this mineral. Its occurrences in Cripple Creek, Colorado, was described by A. H. Chester; and in Kalgoorlie, Western Australia, by A. Frenzel, E. F. Pittman, A. Gmehling, M. Maryansky, and K. Schmeisser. J. A. Krenner called it *bunsenine*—after R. Bunsen—and J. D. Dana altered this to *bunsenite;* while G. vom Rath called it **krennerite** because the former term was already in use for native nickelous oxides. The analysis approximates to **silver**

gold ditelluride, $Ag_2Te.Au_2Te_3$, or $AgAuTe_2$, or, as E. S. Simpson writes it, $(Ag, Au_2)Te_4$, Ag.Te.Te.Te.Te.Au. Analyses were reported by M. H. Klaproth, W. Petz, S. Koch, E. H. Liveing, R. Scharizer, L. Sipöcz, A. H. Chester, A. Frenzel, and E. F. Pittman; the analysis by L. Sipöcz was eq. to $Ag_3Au_{10}Te_{26}$. Krennerite occurs in prismatic crystals which are vertically striated. The colour varies from silver-white to brass-yellow. G. vom Rath found that the rhombic crystals have the axial ratios $a:b:c=0·94071:1:0·50445$. Observations on the crystals were made by A. H. Chester, J. A. Krenner, A. Schrauf, L. Sipöcz, and H. A. Miers. The (001)-cleavage is complete. W. M. Davy and C. M. Farnham examined the etched polished surfaces. W. Petz gave 8·27–8·33 for the sp. gr.; A. Frenzel, 8·14; L. Sipöcz, 8·3533. The hardness is 2·5. H. E. McKinstry observed no action when krennerite is exposed to the electric arc-light. R. G. Harvey measured the electrical resistance.

The *Schrifterz*, *Blättererz*, *aurum graphicum*, etc., indicated in connection with the history of tellurium, to which the term **sylvanite**—from Transylvania—was subsequently applied, was analyzed by M. H. Klaproth,[8] J. J. Berzelius, W. Petz, S. Koch, A. Schrauf, L. Sipöcz, F. W. Clarke, P. Krusch, A. Carnot, E. H. Liveing, C. Palache, W. H. Hobbs, F. A. Genth, V. Hanko, and E. S. Simpson. The results agree with the formula $(Au,Ag)Te_2$, in which the at. ratio Au : Ag varies from 1 : 1 to about 6 : 1. The formula $(Au,Ag)Te_2$ was given by G. Rose, and P. Groth. C. F. Rammelsberg, W. Petz, and C. F. Rammelsberg supposed sylvanite to be a mixture of silver monotelluride and gold tritelluride. G. A. Kenngott used the formula $(Au,Ag,Pb)\ (Te,Sb)_2$. The occurrence of the mineral in Nagyag, Offenbanya, Zalathna, and Faczelraja, Transylvania, was described by B. von Cotta, V. von Zepharovich, A. von Groddeck, A. Schrauf, A. Stütz, K. Vrba, and F. Beyschlag; in Hungary, by F. von Richthofen; in California, by J. D. Mathewson, H. J. Burkart, and G. Küstel; in Colorado, by B. Silliman, F. A. Genth, E. P. Jennings, J. D. Dana, C. Palache, W. F. Hillebrand, R. Pearce, and W. H. Hobbs; in South Dakota, by F. C. Smith; in Ontario, Canada, by G. C. Hoffmann; and in Western Australia, by A. Frenzel, and E. S. Simpson.

The mineral occurs in steel-grey to silver-white crystals with more or less of a yellow tinge. J. C. L. Schröder van der Kolk said that the streak of sylvanite is bluish. The crystals were supposed by W. Phillips, and F. Mohs to be rhombic; and J. F. L. Hausmann, and W. H. Miller inclined to the same view. According to N. V. Kokscharoff, the crystals are monoclinic; this view was supported by J. A. Krenner, and A. des Cloizeaux. According to A. Schrauf, the monoclinic crystals have the axial ratios $a:b:c=1·63394:1:1·12653$, and $\beta=89°\ 35'$. Twinning occurs about the (101)-plane, and there is contact twinning, lamellar twinning, and penetration twinning which give rise to branching dendritic forms resembling written characters—hence the terms *Schrifterz*, and *Schrifttellur*. The dendrites usually cross at an angle of 69° 44′—rarely at 55° 8′, or 90°. Skeleton forms are common. The (010)-cleavage is perfect. The crystals were examined by G. Rose, V. von Zepharovich, F. A. Genth, W. H. Hobbs, C. Palache, etc. W. M. Davy and C. M. Farnham examined etched polished surfaces. The sp. gr. given by W. Petz is 8·28; L. Sipöcz, 8·0733; V. Hanko, 8·036; F. A. Genth, 7·943; and C. Palache, 8·161. The hardness is 1·5. J. Joly observed a sublimate of tellurium dioxide is formed below 730° and 780°; and of monoxide between 460° and 520°. E. T. Wherry formed the mineral to be a fair radio-detector. H. E. McKinstry observed no effect by exposing the mineral to the electric arc-light. R. G. Harvey measured the electrical resistance.

W. H. Hobbs described a mineral from Arequa Gulch, Colorado, which he called *goldschmidtite*—after V. Goldschmidt. It occurs in silvery white, monoclinic prisms with the axial angles $a:b:c=1·8561:1:1·2980$, and $\beta=89°\ 11'$. Twinning is common; the (010)-cleavage is perfect; the sp. gr. is 8·6; and the hardness 2. The analysis corresponded with $AgAu_2Te_6$. C. Gastaldi gave $(Au,Ag)_2Te_5$. In view of the variations in the composition of sylvanite, both C. Palache, and E. S. Simpson consider goldschmidtite to be identical with sylvanite.

F. A. Genth found a pale bronze-yellow, massive, indistinctly crystalline mineral in Calaveras Co., California, and in the Red Closed Mine of Colorado ; he called it **calaverite.** Analyses were reported by A. Carnot, F. A. Genth, W. F. Hillebrand, R. W. E. MacIvor, A. G. Holroyd, P. Krusch, E. H. Liveing, W. Lindgren and F. Ransome, S. L. Penfield and W. E. Ford, L. J. Spencer, E. S. Simpson, etc. The composition corresponds with that of krennerite, $(Au,Ag)Te_2$, or in the idealized case, $AuTe_2$. The crystals were stated by S. L. Penfield and W. E. Ford to be monoclinic with the axial ratios $a:b:c=1\cdot6313:1:1\cdot1449$, and $\beta=90°\ 13'$. G. F. H. Smith regarded it as triclinic with the axial ratios $a:b:c=2\cdot0013:1:1\cdot1743$, and $\alpha=83°\ 58'$, $\beta=100°\ 39'$, and $\gamma=90°\ 19'$. M. L. Huggins studied the electronic structure of the crystals. F. A. Genth gave 9·043 for the sp. gr. ; E. S. Simpson, 9·311 ; J. C. H. Mingaye, 9·377 ; and R. W. E. MacIvor, 9·314 ; J. Joly observed a sublimate of tellurium monoxide occurs between 450° and 530°, and of dioxide between 600° and 675°. A. Beutell obtained moss gold by heating the telluride in a sealed tube at 350°–600°. E. T. Wherry found the mineral to be a fair radio-detector. According to L. J. Spencer, when calaverite is heated on charcoal in the oxidizing flame of the blowpipe, the tellurium it contains is readily oxidized, giving rise to the flame, a bead of gold being left behind. When heated in a bulb-tube, calaverite gives a black sublimate of metallic tellurium, and a less volatile sublimate of drops of tellurous oxide (TeO_2), which is yellow when hot and white or colourless when cold ; a yellow malleable bead of gold is not obtained in this way. During the cooling of the beads so obtained, either on charcoal or in the bulb-tube, the interesting phenomenon of recalescence was sometimes observed —after a red-hot bead had become dark it suddenly and momentarily again flashed out red and glowing. This behaviour, which was also exhibited by beads obtained from sylvanite, appeared to depend on the presence of a small amount of tellurium still remaining in the bead. H. E. McKinstry observed no effect when the mineral is exposed to the electric arc-light. R. G. Harvey studied the electrical resistance.

These observations make it appear as if there are three gold tellurides : (1) idealized **gold ditelluride,** $AuTe_2$—namely, rhombic krennerite ; (2) monoclinic sylvanite, and (3) triclinic calaverite. All these minerals contain more or less silver. The thermal diagram for the system : Au–Te was examined by H. Pélabon, and more completely by G. Pellini and E. Quercigh, whose results are summarized in Fig. 16. The alloys were made by direct fusion in an atm. of carbon dioxide. The curve has a single maximum corresponding with gold ditelluride, $AuTe_2$, melting at 464° ; H. Pélabon gave 472° for the m.p. ; and T. K. Rose, 452°. The curve of G. Pellini and E. Quercigh shows two eutectics at 416° with 12 at. per cent. Au, and at 447° with 47 at. per cent. Au. There is no indication of the formation of solid soln. Since the ditelluride cannot be obtained by the action of tellurium on gold salts, it is inferred that the minerals have been formed by fusion processes. M. Coste's observations on the microscopic appearance and the e.m.f. of gold-tellurium alloys showed the gold telluride.

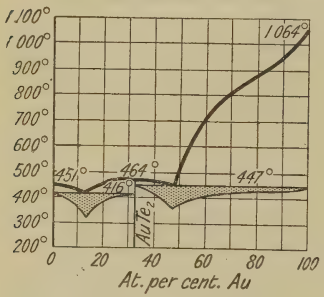


FIG. 16.—Freezing-point Curve of the System : Au–Te.

E. H. Liveing described a white mineral with a bismuth tinge of colour from Kalgoorlie, West Australia. He called it *speculite.* It has the perfect cleavage of sylvanite and a sp. gr. of 8·64. The analysis indicates 36·1 to 36·6 per cent. of gold, 3·50 to 4·45 per cent. of silver, and the rest tellurium.

J. J. Berzelius reported **gold hemitelluride,** Au_2Te, to be formed by heating gold sulphotelluride, $Au_2S_3.TeS_2$, so as to drive off the sulphur ; B. Brauner[9] said that when the alloys of tellurium are heated to redness in a current of carbon dioxide, they dissociate into a mixture of the hemitelluride and gold. J. Margottet said that the hemitelluride is formed when the vapour of tellurium is passed over leaf gold heated in the absence of air. V. Lenher was unable to prepare a gold telluride by heating a mixture of the two elements; and when hydrogen telluride is passed into a soln. of auric chloride, gold is precipitated. If a soln. of auric chloride be treated with tellurium, gold is deposited and tellurium tetrachloride is formed: $4AuCl_3+3Te=4Au+3TeCl_4$. He also found that the natural tellurides—calaverite, sylvanite, coloradoite, kalgoorlite, and nagyagite—the gold-tellurium alloys behave in a similar manner. Hence, it was inferred that these tellurides are not to be regarded as chemical individuals. L. Nowack observed that the alloys with gold and tellurium are very brittle. C. A. Tibbals found that sodium telluride precipitates gold and tellurium from soln. of sodium tellurate, but the substances formed do not appear to be of constant composition. When sodium telluride reacts with an excess of neutral auric chloride soln., a precipitate of metallic gold is formed which contains no tellurium. This may be due to one of two reactions, *viz.* a telluride of gold may be formed which at once reacts with the excess of nitric chloride, reducing it in a manner similar to the action of the natural tellurides; or the sodium telluride may act simply as a reducing agent toward the auric chloride according to the equation: $2AuCl_3+Na_2Te=2NaCl+TeCl_4+2Au$. A. Brukl obtained **auric telluride,** Au_2Te_3, by the action of hydrogen telluride on an ethereal soln. of auric chloride since in aq. soln. the compound is decomposed. The black, flocculent telluride is soluble in soln. of ammonium hydrotelluride and sodium telluride, and only slightly soluble in soln. of ammonium sulphide or sodium sulphide. Non-oxidizing acids are without action, but nitric acid dissolves the tellurium and leaves the gold behind.

The mineral hessite, in the idealized case, is silver hemitelluride, Ag_2Te, but it is nearly always auriferous, and to distinguish the two, J. F. L. Hausmann called the former *Tellursilber* and the latter, *Tellurgoldsilber;* and W. Haidinger proposed to call the auriferous varieties **petzite**—after W. Petz. The analyses and occurrences are included in the description of hessite. Like hessite it crystallizes in the cubic system. The idealized mineral can be regarded as gold hemitelluride, Au_2Te, actually it is a silver gold hemitelluride, $(Au,Ag)_2Te$. J. Joly found that a sublimate of tellurium dioxide is formed at 750°. E. T. Wherry found the mineral to be a poor radio-detector. According to L. J. Spencer, when heated on charcoal in the oxidizing flame of the blowpipe, petzite produces only slightly the bluish-green coloration of the flame and the dense white fumes characteristic of tellurium; only when fused with sodium carbonate does it give a white malleable bead, and this when placed in nitric acid becomes yellow. Calaverite and sylvanite, on the other hand, are much less stable, and are readily converted into a bead of gold by simply heating on charcoal in the oxidizing flame; this, however, takes place much more readily with calaverite than with sylvanite, since the latter contains more silver in combination with the tellurium. H. E. McKinstry observed no effect by exposing the mineral to the electric arc-light. According to F. Zambonini, the analyses of krennerite fall into two groups: those containing but little silver and with the ditelluride formula $(Au,Ag)Te_2$; and those containing about 20 per cent. silver, which have the monotelluride formula $(Ag,Au)Te$. Crystals of the former group are identical with the orthorhombic krennerite; and those of the latter group are taken to represent a distinct species for which the name **muthmannite**—after W. Muthmann—was proposed. Analyses by A. Schrauf, S. Koch, R. Scharizer, and C. Gastaldi agree with the formula for **silver gold monotelluride,** $(Au,Ag)Te$, or in the idealized case, **gold monotelluride,** $AuTe$. Externally, muthmannite resembles krennerite, but the imperfect crystals are tabular and often elongated in one direction, parallel to which direction there is a perfect cleavage. The colour is very pale brass-yellow, but on a fresh cleavage, greyish-white. A. D. Alvir described a gold silver telluride from Antamok, Philippine Islands, which he called *antamokite*.

M. Berthelot and C. Fabre[10] obtained **calcium telluride,** presumably $CaTe$, by heating calcium tellurite with carbon in a current of hydrogen. It is decomposed by acids with the evolution of hydrogen telluride, rapidly if the telluride is powdered, and slowly if it be in lumps. M. Berthelot and C. Fabre obtained **strontium telluride** in a similar way; and also **barium telluride.** F. A. Henglein and R. Roth could not make the alkaline earth tellurides by the methods they used for the selenides. M. Haase gave 4·87 for the sp. gr. and 54·41 for the mol. vol. of calcium telluride; respectively 5·22 and 41·21 for strontium telluride; and respectively 5·51 and 48·08 for barium telluride. The X-radiograms show that the space-lattices of calcium and strontium tellurides have the sodium chloride structure with a respectively 3·20 A., and 3·34 A. V. M. Goldschmidt gave $a=6·343$ A. for calcium telluride, and I. Oftedal, $a=6·345$ A., while M. Haase gave $a=6·82$ to 6·86 A. for barium telluride, 6·48 A. for strontium telluride, and 6·1 A. for calcium telluride. He also gave for the ionic distances 3·05 A. for calcium telluride, 3·26 A. for strontium telluride, and 3·41 A. for barium telluride. L. Pauling discussed the structure. K. Spangenberg found the crystal structure of barium telluride to be of the sodium chloride type with a density of 7·593. He also found the index of refraction and the mol. refraction to be respectively 2·51, and 22·04 for calcium telluride; 2·408, and 25·39 for strontium telluride; and 2·440, and 29·94 for barium telluride. I. Oftedal discussed the lattice constants of calcium telluride. M. Haase found the index of refraction for the D-line to be between 2·51 and 2·58 for calcium telluride; and for the Tl-, D-, and C-lines respectively 2·460, 2·448, and 2·367 for strontium telluride, and 2·520, 2·440, and 2·379 for barium telluride. For the mol. refraction of calcium, strontium, and barium tellurides, he gave respectively 21·99, 24·38, and 29·95. F. Wöhler prepared **beryllium telluride,** as a grey powder, by heating a mixture of the two elements. Combination occurs without incandescence; and the cold product gives off hydrogen telluride when treated with water. W. Zachariasen gave $a=5·615$ A. for the side of the face-centred lattice of beryllium telluride. M. Berthelot and C. Fabre obtained **magnesium telluride,** presumably MgTe, by heating magnesium in the vapour of tellurium carried by a current of hydrogen. If a mixture of tellurium and magnesium be heated to dull redness, a reaction sets in with explosive violence. W. Zachariasen found that while magnesium oxide, sulphide and selenide have the sodium chloride structure, magnesium telluride has the wurtzite space-lattice with side $a=4·52$ A., $c=7·33$ A., and $a:c=1:1·622$; the calculated density is 3·86, and the shortest distance between the magnesium and tellurium atoms is 2·76 A. M. Haase gave 26·83 for the mol. vol. K. Spangenberg found the index of refraction to be 3·05, and the mol. refraction 29·94; while M. Haase gave 3·50 for the index of refraction for the D-line. White, flocculent magnesium telluride quickly turns brown when exposed to air, it dissolves in water forming a purple-red soln. if the water is only slightly aërated, but if the water is charged only with nitrogen, the aq. soln. is colourless. Acidulated water acts on the telluride with the evolution of hydrogen telluride. L. Moser and K. Erth prepared magnesium telluride, as a brown sintered mass, by distilling tellurium at a low press. over finely-divided magnesium. D. M. Liddell made it by dropping tellurium into molten magnesium. According to A. Hilger, and K. B. Heberlein, an ammoniacal soln. of a magnesium salt in the presence of an aq. soln. of an alkali telluride gives a precipitate of **ammonium magnesium telluride.**

J. J. Berzelius[11] found that when a mixture of zinc and tellurium is heated union occurs with incandescence, and a grey porous, crystalline mass is produced which is not soluble in dil. sulphuric acid or conc. hydrochloric acid. J. Margottet obtained **zinc telluride,** ZnTe, by heating a mixture of the component elements; and C. A. Tibbals obtained it in a similar way. M. Kobayashi found that alloys of tellurium and zinc furnish a f.p. curve, Fig. 17, which shows the existence of only one compound, ZnTe, with a maximum at 1238·5°. The two eutectic points practically coincide with the m.p. of the pure components. The f.p. curve falls steadily from the compound to tellurium, but alloys richer in zinc lose zinc so rapidly by volatilization that it is not possible to determine the course of the curve, although the zinc eutectic arrest is well marked. H. St. C. Deville and L. Troost obtained cubic crystals of the telluride by passing hydrogen over zinc telluride heated to bright redness. L. Moser and K. Erth prepared zinc telluride, as a pale brown mass, stable in air, by distilling tellurium at a low press. over finely-divided zinc. E. Kordes studied the eutectic. M. Kobayashi obtained the telluride as a mass of microscopic needles of sp. gr. 5·54 at 13°. W. Zachariasen found that the X-radiograms indicate that the cubic space-lattice, of the zinc blende type, has four mols. per cell; the edge-length of the cells is 6·07 A.; and the calculated density is 5·72. By a double decomposition of soln. of sodium telluride and zinc acetate in acetic acid soln., C. A. Tibbals obtained a yellowish-brown precipitate of the *monohydrate*, $ZnTe.H_2O$; this turns brown when dried. The compound was also prepared by A. Brukl. F. Henglein gave 29·5 for the mol. vol. M. L. Huggins studied the atomic structure of the crystals. W. Zachariasen gave $a=6{\cdot}089$ A. for the side of the face-centred lattice. It is decomposed by dil. hydrochloric acid; it is oxidized by nitric acid; and unaffected by dil. sulphuric acid; it gives the dark red anhydride when heated out of contact with air. C. Fabre gave 37·22 Cals. for the heat of formation of the crystalline telluride.

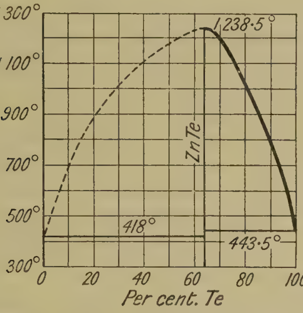


FIG. 17.—Freezing-point Curve of the System: Zn–Te.

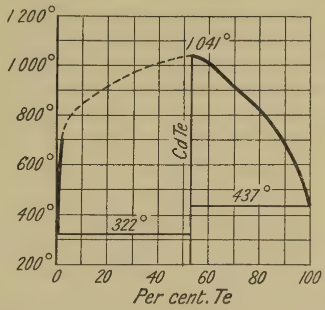


FIG. 18.—Freezing-point Curve of the System: Cd–Te.

A. Oppenheim obtained impure **cadmium telluride,** CdTe, by heating cadmium tellurite or tellurate to redness in a current of hydrogen. The black powder yields a porous, grey mass when heated more strongly. J. Margottet prepared this compound by melting together eq. proportions of the two elements at 500°, and subliming the product slowly in a current of hydrogen. M. Kobayashi made alloys by fusing mixtures of the two elements in glass or porcelain tubes in an atm. of carbon dioxide. The f.p. curve, Fig. 18, has a maximum at about 1041°, corresponding with the compound TeCd, but it is not possible to prepare this compound in a pure condition under ordinary press., owing to the volatility of cadmium. The two eutectic points lie so near to the f.p. of cadmium and tellurium respectively as to be indistinguishable from them. W. Zachariasen found that the X-radiogram agrees with a cubic space-lattice, containing four mols. per cell which is of the zinc blende type with the edge-length of the cell 6·41 A.; and the density, 6·06. W. Hartvig also said that the space-lattice is of the zinc blende type. C. A. Tibbals, and A. Brukl obtained the telluride by treating a soln. of cadmium in acetic acid with sodium telluride. M. L. Huggins studied the atomic structure of the crystals. C. Fabre gave for the heat of formation: (Cd,Te)=20 Cals. C. A. Tibbals said that the chestnut-brown precipitate dries almost black; it is easily oxidized by moist air; and is very resistant towards acids; nitric acid alone attacks it in the cold. A. Brukl observed no sign of the complex $2CdTe.CdCl_2$.

F. A. Genth[12] described an iron-black mineral which occurs at Keystone, Colorado, and which he called **coloradoite.** The analysis was made on impure samples, but the results were taken by F. A. Genth, and C. F. Rammelsberg to indicate that idealized coloradoite is **mercury monotelluride,** HgTe, mixed with native tellurium. E. S. Simpson analyzed a sample from West Australia and gave the representative formula Hg_2Te_3; but L. J. Spencer found that selected samples of homogeneous material from the same locality gave results in agreement with the monotelluride formula. L. Rivot, and G. A. Kenngott described impure mercury telluride from Chili: and W. F. Hillebrand, from California. The mineral occurs massive and granular. L. J. Spencer thus described the mineral from West Australia. It is iron-black, opaque, with a bright metallic lustre, an excellent conchoidal fracture, but no indication of cleavage. W. Zachariasen found that the X-radiogram of the monotelluride agrees with a cubic space-lattice, of the zinc blende type, with four mols. per cell; the edge-length of the cell is a=6·36 A.; and the calculated density is 8·42. F. de Jong found a=6·43 A.; density 8·20; and the distance between the mercury and tellurium atoms 2·78 A. M. L. Huggins studied the atomic structure of the crystals. The mineral is brittle and extremely friable. W. M. Davy and C. M. Farnham studied the etching of polished surfaces of the mineral. For impure samples, F. A. Genth gave 8·627; and E. S. Simpson, 9·21; but for more pure samples, L. J. Spencer gave 8·062 to 8·077—mean, 8·07. According to L. J. Spencer, tetrahedral cubic crystals of metacinnabarite, HgS, have a sp. gr. 7·81; those of tiemannite, 8·19; but coloradoite, instead of having a greater sp. gr. has a smaller one. F. Henglein gave 38·0 for the mol. vol. J. Joly observed a sublimate of tellurium monoxide occurs at 20°, and of the dioxide at 835°. F. A. Genth gave for the hardness, 3·0; L. J. Spencer, 2·5. F. Beijerinck, and R. D. Harvey said that it is a good conductor of electricity; and E. T. Wherry found it to be a fair radio-detector. P. I. Wolf and J. M. Hyatt studied the Hall effect with tellurium amalgams. L. J. Spencer said that when coloradoite is heated on charcoal, it readily fuses and colours the flame bright bluish-green, emits dense white fumes, and in a very short time completely disappears. In the closed tube it fuses with spluttering to a black globule, and gives a sublimate of globules of mercury and a much less volatile sublimate of drops of tellurous oxide, the latter being yellow when hot and white or colourless when cold; with a larger fragment of material a black sublimate of metallic tellurium is also obtained.

Both M. H. Klaproth, and J. J. Berzelius noted the ease with which tellurium amalgamates with mercury, and they prepared tin-white, and granular *tellurium amalgams;* and G. Pellini and C. Aureggi found that mixtures of mercury and powdered tellurium react readily on heating with development of a considerable amount of heat. When 66 at. per cent. or more of tellurium are present, the mixture fuses completely, whilst mixtures less rich in tellurium decompose at a high temp. with liberation of mercury. The solidification curves of mixtures containing from 60 to 65 at. per cent. of tellurium exhibit a eutectic temp. halt at about 410°, Fig. 19. The form of the curves indicates the existence of a mercuric monotelluride, which, however, melts with decomposition at the ordinary press., its upper limit of stability being about 550°. The eutectic Te+HgTe corresponds with 87 at. per cent. of tellurium, and has a distinctly crystalline appearance. Tellurium dissolves only slightly in mercury. When triturated in a mortar at the ordinary temp., mercury and tellurium yield a greyish-white paste with a metallic lustre, from which, after a long time, or by gently heating, the monotelluride may be isolated. A. C. Vournasos obtained the monotelluride by heating the constituents under melted paraffin. J. Margottet found that the

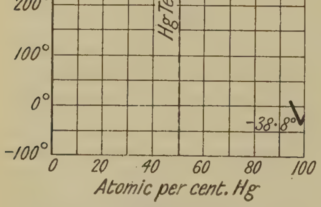


FIG. 19.—Freezing-point Curve of the System: Hg–Te.

vapours of the two elements at about 800° unite with a small explosion, with the evolution of heat. The black powder which is formed suffers a little dissociation at 360°. F. Krafft and R. E. Lyons obtained the telluride by the action of tellurium dichloride on mercury phenide. C. A. Tibbals observed that sodium telluride soln. precipitates from mercuric chloride soln., a grey substance, which changes first to a yellow and then to a red colour, and finally to a homogeneous light brown. The final product is mercurous chloride, and tellurium is found to be dissolved in the soln. Mercuric telluride is probably formed at first, but subsequently reacts with the excess of mercuric chloride reducing it to mercurous chloride with the formation of tellurium chloride. A. Brukl obtained it by the action of hydrogen telluride on soln. of mercuric salts. Mercury monotelluride is not stable in air, but readily decomposes into its components. It is a little soluble in a mixed soln. of sodium sulphide and hydroxide, but not in ammonium sulphide; it is a little soluble in a soln. of ammonium hydrotelluride. Mercuric chloride soln. are reduced. Mercuric telluride is easily oxidized by nitric acid, and acids decompose it into its elements without forming hydrogen telluride. A. Brukl could not prepare *mercurous telluride*, Hg_2Te, by the action of hydrogen telluride on a soln. of a mercurous salt The product is a mixture of tellurium and mercury.

E. F. Pittman described an iron-black mineral from Kalgoorlie, West Australia, and he called it *kalgoorlite*. The analysis corresponded with $HgAu_2Ag_6Te_6$; and the sp. gr. was 8·791. E. S. Simpson, and L. J. Spencer also analyzed a sample with results in agreement with this. A. Carnot previously applied the term kalgoorlite to a mercurial petzite from the same locality. T. A. Richard, and E. H. Liveing regarded it as a mixture of petzite and coloradoite; and this was proved to be the case by L. J. Spencer—thus, $HgAu_2Ag_6Te_6 = HgTe(\text{coloradoite}) + 2Ag_3AuTe_2(\text{petzite}) + Te$. H. E. McKinstry observed no effect when the mineral is exposed to the electric arc-light. A. Carnot also described a mineral from the East Coolgardie gold field, West Australia, as a sesquitelluride of gold, silver, and mercury, $(Au, Ag, Hg, Cu, Fe, Sb)_2Te_3$, or $(Au, Ag, Hg)_2Te_3$. It was called **coolgardite.** The analyses differ widely, and L. J. Spencer showed that coolgardite is probably not a distinct, homogeneous individual, but rather a mixture of coloradoite, calaverite, petzite, and sylvanite.

H. Moissan[13] observed that boron does not combine with tellurium to form a *boron telluride*. F. Wöhler prepared presumably normal **aluminium telluride,** Al_2Te_3, by heating a mixture of the powdered elements; a vigorous reaction sets in, with incandescence. M. Chikashige and J. Nosé made a similar observation. C. Whitehead said that this telluride is formed when variable quantities of the two elements are melted together. D. M. Liddell made the telluride by dropping tellurium into molten aluminium. R. de Forcrand and H. Fonzes-Diacon inflamed a mixture of the powdered elements by means of a piece of magnesium ribbon. M. Chikashige and J. Nosé studied the f.p. curve of the mixtures, and their results are summarized in Fig. 20. The f.p. curve on the tellurium side shows the formation of the normal telluride Al_2Te_3, of m.p. 895°. This telluride forms mixed crystals with tellurium, the series extending from the pure compound (12·4 per cent. by weight of aluminium) to a mixture which contains 4·4 per cent. of aluminium. On cooling, the α-mixed crystals undergo transformation into β-mixed crystals. The temp. at which this conversion takes place diminishes with increase in the tellurium content, and for the sat. α-mixed crystals falls to 541°. The β-mixed crystals and tellurium co-exist at the eutectic temp. 414°, the eutectic mixture containing 2·8 per cent. of aluminium. L. Moser and K. Erth prepared aluminium telluride as a blackish-brown, amorphous mass, by passing the vapour of tellurium, under

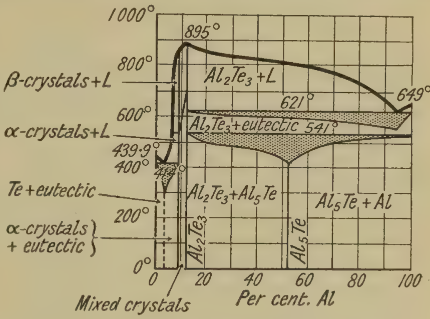


Fig. 20.—Freezing-point Curves of Mixtures of Aluminium and Tellurium.

reduced press., over finely-divided aluminium. A. L. Pocock and co-workers discussed the preparation of Al-Te-alloys. The telluride may appear as a black, brittle mass with a metallic appearance, or it may be a chocolate-brown powder. It smells of hydrogen telluride, and gives off that gas vigorously when treated with water or in contact with moist air: $Al_2Te_3+3H_2O=3H_2Te+Al_2O_3$. L. Moser and K. Erth also said that aluminium telluride decomposes in air forming hydrogen telluride; and they recommended the dropping of aluminium telluride into dil. acid as a mode of preparing hydrogen telluride. G. Natta studied the action of the telluride on alcohols and ethers. The f.p. curve of mixtures of aluminium and tellurium on the aluminium side of the Al_2Te_3-curve is terminated by a eutectic point, in which the telluride and aluminium co-exist in equilibrium. The eutectic mixture contains 97 per cent. of aluminium and the eutectic temp. is 621°. The conglomerates, consisting of the telluride or aluminium and the eutectic, undergo transformation when the temp. has fallen to 551° with the formation of **aluminium pentitatelluride,** Al_5Te, according to the equation: $Al_2Te_3+13Al=3Al_5Te$. The compound Al_5Te is less readily decomposed, but hydrogen telluride is liberated in contact with water, the reaction being possibly represented by $Al_5Te+H_2O+O_2=TeH_2+Al_2O_3+3Al$. F. T. Sisco and M. R. Whitmore studied some ternary alloys of aluminium, copper, and tellurium.

According to C. Renz,[14] indium and tellurium unite with incandescence when the mixture is heated forming, presumably, **indium telluride,** In_2Te_3. According to H. Pélabon, tellurium unites with thallium when the two elements are melted together, forming **thallium hemitelluride,** Tl_2Te, when more than 24 per cent. of Tl is present. A. Brukl prepared this telluride by the action of hydrogen telluride on an ammoniacal soln. of a thallous salt. It is easily decomposed, and gives hydrogen telluride with acids. C. Fabre gave 12·24 for the heat of formation of crystallized thallous telluride. G. Tammann studied the chemical activity of the alloys. This compound melts at 412°, and as the proportion of thallium diminishes, the m.p. curve rises to a maximum at 422°, corresponding with the compound **thallium pentitatritelluride,** Tl_5Te_3, or $Tl_2Te_3.9Tl_2Te$. The curve then falls to a minimum at 214° representing, presumably, the eutectic mixture $2Tl+5Te$; and it finally rises to 452°, the m.p. of tellurium alone. M. Chikashige's f.p. curve, Fig. 21, shows only a single maximum at 428° corresponding with **thallium tritaditelluride,** Tl_3Te_2, and the break in the curve at 305° and 40·5 per cent. of tellurium corresponds with **thallium monotelluride,** TlTe. The eutectic point lies at 200° and 58·5 per cent. Te. The alloys separate into two liquid layers between the limits 1·5 and 24 per cent. Te at 393°. Solid soln. are formed only by the compound Te_2Tl_3 with 5·5 per cent. of thallium. This compound is very brittle, whilst the compound TeTl, which forms long needles, is much less so.

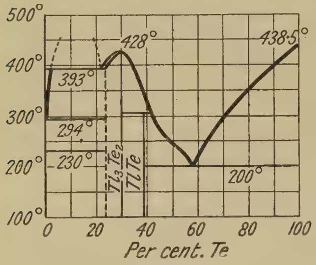


FIG. 21.—Freezing-point Curve of the System: Tl–Te.

According to A. Stock and H. Blumenthal,[15] when an arc is formed under carbon disulphide between a tellurium cathode and a graphite anode the tellurium is rapidly vaporized, and condenses, for the most part, in the form of a fine black powder. At the same time the carbon disulphide becomes yellow to brownish-red in colour, and acquires a penetrating, very disagreeable odour. On exposure to daylight, the filtered soln. soon, and in direct sunlight immediately, deposits a black precipitate. If the yellow soln. is concentrated by evaporation on the water-bath, and then heated in a sealed evacuated tube at 175° for forty-eight hours, a greyish-black deposit is obtained, the carbon disulphide not being affected. Analyses agreed with the assumption that the unstable compound dissolved in carbon disulphide, and which is readily decomposed by exposure to light or heat, is **carbon ditelluride,** CTe_2. On evaporating the yellow soln. in carbon disulphide, it leaves a viscid, brown residue, which will again dissolve to a yellow soln. if immediately treated with the solvent, but otherwise becomes solid and greyish-black in a few seconds, decomposing into carbon and tellurium. The same soln. at —100° gives glistening, brown crystals, which dissolve on slightly raising the temp. The soln. of carbon telluride has an unbearable penetrating odour, even when so dilute as 0·1 per cent. Smelling a somewhat stronger soln. for only a short time is enough to impart an intense odour of garlic to the breath for several days. A. Stock and P. Praetorius showed that the phenomena are due to the decomposition of carbon sulphotelluride—*vide infra.* There is no evidence that carbon ditelluride has been prepared. I. Oftedal prepared small, tabular, red crystals of **titanium telluride,** $TiTe_2$, by heating a mixture of powdered titanium and tellurium. The X-radiograms show that the crystals have a structure like cadmium iodide-stannic sulphide, and titanium sulphide and selenide. The hexagonal lattice has $a=3·774$ A., and $c=6·539$ A., or $a:c=1:1·732$. The calculated sp. gr. is 6·24. G. Natta, and V. M. Goldschmidt studied this subject. J. J. Berzelius observed that tellurium readily alloys with tin, and A. Ditte found that **tin monotelluride,** or **stannous telluride,** SnTe, is produced when the two elements in theoretical proportions are melted together. Combination occurs with incandescence as soon as the tin melts. If the matte-grey powder be heated to bright redness in a current of hydrogen, it forms a green vapour, and slowly distils. D. M. Liddell made the alloy by dropping tellurium into molten tin. H. Pélabon found that the f.p. curve of tin rises with the addition of tellurium rapidly and then more gradually until a maximum at 780° is attained corresponding with the monotelluride; the curve then falls rapidly to a minimum curve at 388°, the f.p. of the eutectic with 17 per cent. of tellurium. It then rises to 452°, the m.p. of tellurium. There is no sign of either Sn_2Te_3 or of $SnTe_2$ on the f.p. curve. In H. Fay's curve, the maximum for SnTe is at 769°, and the eutectic at 399° and 85 per cent. Te; the other eutectic has a very low proportion of tellurium. In W. Biltz and W. Mecklenberg's curve, Fig. 22, the maximum for SnTe is at 800°, and a eutectic at 404° and 85 per cent. Te. M. Kobayashi obtained a maximum at 780°, and a eutectic at 393° with 86 per cent. of tellurium. E. Kordes studied the eutectics. A. Brukl obtained stannous telluride, SnTe, by the action of hydrogen telluride on a soln. of stannous chloride. W. Harz gave $3·07\times10^{12}$ for the vibration-frequency. W. Haken's observations on the electrical conductivities of the alloys are summarized in Fig. 23; and his observations on the thermoelectric powers are summarized in Fig. 24. Well-dipped breaks occur corresponding with the monotelluride. Between 55 and 100 per cent. of Sn, the

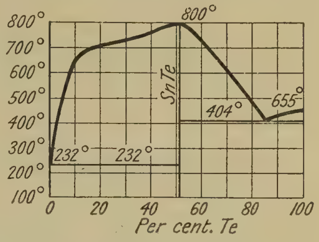


FIG. 22.—Freezing-point Curve of Tin and Tellurium.

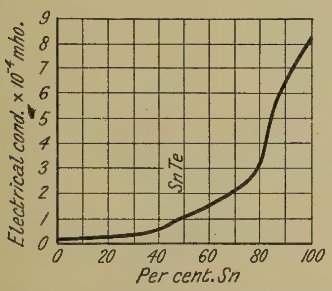


FIG. 23.—The Electrical Conductivities of the Sn–Te Alloy.

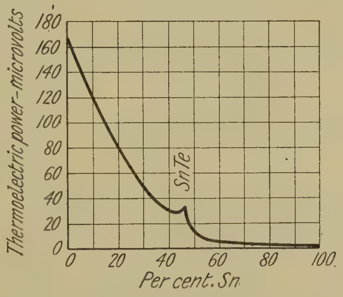


FIG. 24.—The Thermoelectric Powers of the Sn–Te Alloys.

thermoelectric power curve is a straight line of small slope. N. A. Puschin observed that the grey alloys of tellurium and tin are brittle, and that the electrode potential difference with the cell Sn | N-H_2SO_4 | $SnTe_n$ has a break corresponding with the monotelluride, as shown in Fig. 25. The observations of K. Honda and T. Sone on the magnetic susceptibilities of the solid and liquid alloys, are summarized in Fig. 26. The curve consists of two straight lines which intersect at the concentration corresponding with the monotelluride. H. Endo also studied the magnetic properties of the alloy. A. Ditte said that when the monotelluride is heated with a conc. soln. of alkali sulphide, tellurium sulphostannate is not formed, but tellurium separates in fern-like, rhombohedral plates. A. Brukl made **stannic telluride** or **tin ditelluride,** $SnTe_2$, by the action of hydrogen telluride on a soln. of a stannic salt. The black flocculent precipitate is insoluble in water, but it readily dissolves in soln. of ammonium sulphide, or of alkali hydroxide. The latter soln. is red, but it becomes colourless in air with the separation of a grey powder. It is decomposed by dil. acids. G. Tammann studied the chemical activity of the Se-Te alloys.

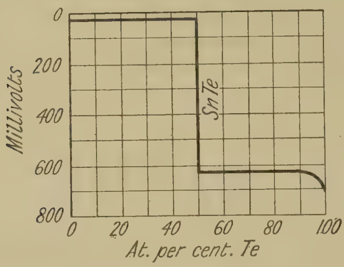


FIG. 25.—Electromotive Force of the Cell Sn | N-H_2SO_4 | $SnTe_n$.

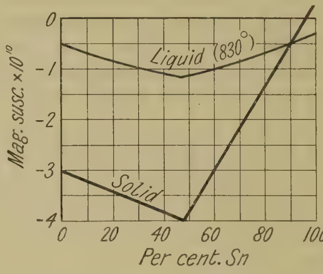


FIG. 26.—Magnetic Susceptibility of the Sn–Te Alloys.

G. Rose[16] obtained a mineral from Altai, Urals, which he described as a telluride of lead; and it was called **altaite** by W. Haidinger. F. S. Beudant employed J. J. N. Huot's term for nagyagite, namely, *elasmose.* H. Louis described its occurrence at Choukpazat, Upper Burma; I. Domeyko, in Condorriaco, Chili; C. A. Stetefeldt, and F. A. Genth, in Calaveras Co., California; W. T. Schaller, Tuolumne Co., California; F. M. Endlich, and F. A. Genth, at Goldhill, Colorado; F. A. Genth, in Gaston Co., North Carolina; G. C. Hoffmann, in Kootanie, and Yale, British Columbia; A. des Cloizeaux, Bontddu, North Wales; and L. J. Spencer, and E. S. Simpson, Kalgoorlie, West Australia. Analyses of altaite were reported by G. Rose, H. Louis, F. A. Genth, G. C. Hoffmann, W. T. Schaller, and E. S. Simpson. The results agree that altaite is a **lead monotelluride,** PbTe, in which a little silver may replace lead, and a little sulphur or selenium may replace tellurium. The mineral usually occurs massive, rarely in cubes.

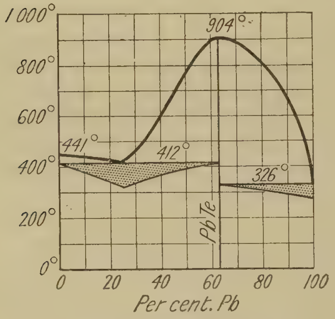


FIG. 27.—Freezing-point Curve of Lead and Tellurium.

J. J. Berzelius observed that lead and tellurium readily form alloys when a mixture of the two elements is melted. H. Fay and C. B. Gillson added tellurium to lead melted under a layer of charcoal; and W. Haken melted the mixture in hydrogen gas. D. M. Liddell made the alloy by dropping tellurium into molten lead. Alloys were also made by M. Dreifuss, N. A. Puschin, C. A. Tibbals, H. Pélabon, A. C. Vournasos, and M. Kimura. J. Margottet said that union occurs at about 500°, and is attended by the evolution of heat and light. C. Fabre made the monotelluride by passing the vapour of tellurium, in a current of nitrogen, over heated lead. C. A. Tibbals obtained PbTe by heating Pb_2Te_3 to redness; and A. Brukl, by adding sodium telluride to a soln. of a lead salt. According to H. Pélabon, the f.p. curve has a maximum at 860° corresponding with the monotelluride and a eutectic at 452° with 9·5 at. per cent. of tellurium. H. Fay and C. B. Gillson added that the lead easily becomes supersaturated with respect to lead telluride, which separates out at the higher f.p., and the lower f.p. then corresponds with the solidification of the lead. When still more tellurium is present, lead telluride again separates at the higher temp., but the lower f.p. corresponds with the complete solidification of the alloy, which is an eutectic of lead telluride and tellurium. According to M. Kimura, the f.p. curve is of the simple type, Fig. 24, with only one compound, PbTe, melting at 904°; there is a eutectic at 412° with 24 per cent. of lead; the other eutectic is practically coincident with pure lead. A. Mazzucchelli and A. Vercillo did not obtain a definite lead telluride by the action of lead on tellurium tetrachloride. E. Kordes studied the eutectics.

The colour of altaite is tin-white, with a yellowish tinge tarnishing to bronze-yellow. The cleavage is cubic. According to N. A. Puschin, the tellurium-lead alloys are grey and crystalline, with a fine-grained fracture. H. Fay and C. B. Gillson said that the microstructure shows a eutectic interspersed with crystals of lead or tellurium according to which is present in excess; and M. Kimura found the microstructure to be in accord with the thermal diagram. C. H. Green studied the Pb–Te eutectics. W. M. Davy and C. M. Farnham examined polished and etched surfaces of altaite. L. S. Ramsdell found that the X-radiogram showed that the face-centred space-lattice is like that of galena; with a=6·34 A. L. Pauling discussed the lattice-structure. G. Rose gave 8·16 for the sp. gr. of altaite; F. A. Genth, 8·060; G. C. Hoffmann, 8·081; and E. S. Simpson, 8·223. F. Henglein gave 40·7 for the mol. vol. H. Fay and C. B. Gillson found that alloys with over 50 per cent. of tellurium are very brittle; and that their hardness increases as the proportion of tellurium increases. According to P. Saldau, the curve of hardness for the system Pb-Te shows for the compound PbTe (altaite) a hardness of 31·85 kg. per sq. mm. considerably in excess of that of either of the components (Pb 3·92, Te 18·43 kg. per sq. mm.). The maximum degree of hardness (33·58 kg. per sq. mm.) corresponds with a content of Te 49·8 at. per cent. In the system PbTe–Pb, lead telluride enters into solid soln. only to a limited extent, whilst in the system PbTe–Te it fails to do so. The m.p. given by H. Pélabon is 860°; and by M. Kimura, 904°. J. Margottet observed that volatilization occurs at a bright red-heat, and cubic crystals deposit in the cold part of the tube. J. Joly observed that a sublimate of tellurium dioxide occurs with altaite at 710° to 850°. C. Fabre gave 11·429 Cals. for the heat formation. E. T. Wherry found altaite to be a poor radio-detector; R. G. Harvey studied the electrical resistance; and T. W. Case observed that light has no measurable effect on the electrical resistance of altaite. W. Haken found that the thermal e.m.f. of the lead-tellurium alloys is a minimum, —70 microvolts, with the monotelluride. N. A. Puschin measured the potential difference with the cell Pb | N-$Pb(NO_3)_2$ | $PbTe_n$, and found a marked break corresponding with the monotelluride; thus,

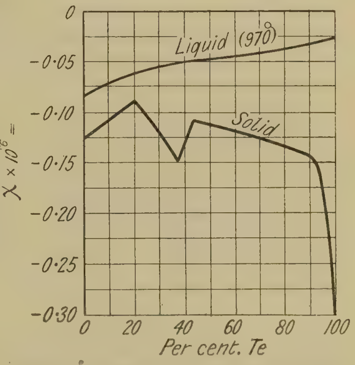


FIG. 28.—Magnetic Susceptibility of the Pb–Te Alloys.

At. per cent. Te .	15	33	46	50	66	100
P.D. in millivolts .	0	50	176	482	485	585

H. Endo, and K. Honda and T. Sone measured the magnetic susceptibility of the solid and liquid alloys, and their results are summarized in Fig. 28. H. Endo also studied the magnetic properties of the alloys. H. Fay and C. B. Gillson found that chlorine passed over the heated alloy forms tellurium tetrachloride which can be distilled off; and C. Fabre said that the heat of soln. in bromine or bromine water is 104·76 Cals. K. B. Rogers found that altaite is decomposed when it is heated in the vapour of carbon tetrachloride.

C. A. Tibbals found that when a soln. of sodium polytelluride is added to a soln. of lead acetate in acetic acid, a heavy black precipitate of hydrated **lead hemitritelluride,** $Pb_2Te_3.4H_2O$, is formed. The *tetrahydrate* is oxidized by nitric acid; but is not attacked by sulphuric and hydrochloric acids; it loses water when heated in a current of hydrogen, fuses, and as the heat is increased, tellurium volatilizes leaving the monotelluride as a residue. G. Tammann studied the chemical activity of the lead-tellurium alloys.

According to R. Metzner,[17] dried liquid ammonia, at —15°, acts on tellurium tetrachloride, so as to form a yellow substance accompanied by an expansion. This product is a mixture of white ammonium chloride and a yellow substance. The solid is washed by decantation, and then with water to get rid of the last traces of ammonium chloride; it is then washed with dil. acetic acid, and finally with water. When dried in vacuo and analyzed, the composition of the lemon-yellow, amorphous mass agrees with **nitrogen monotelluride,** NTe. It explodes when heated to 200°, producing tellurium as a black dust. It is not attacked by water or dil. acetic acid; it is insoluble in liquid ammonia; and with potash-lye, all the nitrogen is evolved as ammonia. The compound was also obtained by M. Damiens. W. Strecker and W. Ebert said that if ammonia acts on tellurium tetrachloride or tetrabromide at —80°, the primary action results in the formation of a hexammine, and this is followed by the gradual replacement of the halogen atoms by the amido-group; then by loss of ammonia into imide and ultimately nitride. The ammonolysis proceeds in accord with $3TeBr_4+4NH_3=Te_3Br_9N+3NH_4Br$; $3TeBr_4+8NH_3=Te_3Br_6N_2+6NH_4Br$; and $TeBr_4+4NH_3=TeBrN+3NH_4Br$. It is supposed that the TeN-compound is really an impure tellurium bromonitride, and that the product is **tellurium tritatetranitride,** Te_3N_4. The ultimate reaction is probably in accord with $3TeBr_4+16NH_3=Te_3N_4+12NH_4Br$. A. Oppenheim[18] observed that a *tellurium phosphide,* or phosphorus telluride, is produced by warming powdered tellurium and phosphorus in a glass tube; but the product has not been investigated.

A. Oppenheim[19] prepared **arsenic telluride,** As_2Te_3, as well as AsTe, in the form of white, brittle alloys, by melting together the constituent elements in these proportions; and similarly E. C. Szarvasy and C. Messinger, an alloy of the composition As_8Te_3. It dissociates when vaporized. It is insoluble in ordinary organic and inorganic solvents; it is not attacked by hydrochloric or sulphuric acid; but fuming nitric acid oxidizes it to arsenic and tellurous acids. There is nothing here to show which of these products is a chemical individual, since by the same method, if two elements form a homogeneous series of alloys, an indefinitely large number of each compounds could be made. H. Pélabon found that the f.p. curve, Fig. 29, had a maximum at 362° corresponding with As_2Te_3. This compound forms a mass of long, silver-white needles with a pale yellow tint. According to C. A. Tibbals, sodium telluride precipitates from aq. soln. of arsenic trioxide a brown arsenic telluride contaminated with tellurium. Arsenic telluride was allowed to stand for several hrs. in contact with a conc. soln. of sodium polytelluride. The soln., after filtration, was dark brown in colour and it contained both arsenic and tellurium. This would seem to indicate the existence of telluro-compounds analogous to the

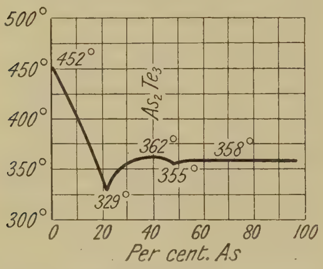


Fig. 29.—Freezing-point Curve of Mixtures of Arsenic and Tellurium.

sulpho-salts. This salt was also prepared by A. Brukl by the action of a feebly acid soln. of arsenic trichloride.

By fusing a mixture of the constituent elements in the correct proportions, A. Oppenheim obtained **antimony telluride**, Sb_2Te_3, as well as SbTe; but as in the case of arsenic, there is nothing to show that chemical individuals were in question. H. Pélabon found a maximum on the f.p. curve corresponding with Sb_2Te_3, and eutectics corresponding with 5Sb : 2Te, and Sb : 10Te. H. Fay and H. E. Ashley also observed a maximum at 629° corresponding with Sb_2Te_3, and a eutectic at 421° corresponding with 87 per cent. Te. The observations of Y. Kimata are summarized in Fig. 30. The maximum at 620° corresponds with Sb_2Te_3; and there are eutectics at 540° with 28 per cent. Te, and at 420° with 89 per cent. Te. There is no indication of the formation of solid soln.; but the flatness of the curve near the eutectic on the bismuth side led H. Fay and H. E. Ashley to assume that solid soln. were formed. N. S. Konstantinoff and V. I. Smirnoff obtained a maximum at 622°, corresponding with Sb_2Te_3, one eutectic at 540° and 30 per cent. Te, and the other at 424° and 89 per cent. Te. They observed no sign of the formation of solid soln. near the antimony end, and only a small region near the antimony telluride. Possibly H. Fay and H. E. Ashley were misled by undercooling phenomena. This salt was also prepared by A. Brukl by the action of hydrogen telluride on a feebly acidic soln. of antimony trichloride. M. Dreifuss made some observations on the properties of these alloys. The measurements of W. Haken on the electrical conductivity of the antimony tellurium alloys are summarized in Fig. 31, and of the thermoelectric power in Fig. 32. M. Padoa observed a maximum in the conductivity corresponding with Sb_2Te_3. E. Becquerel made observations on this subject. The addition of antimony to tellurium causes a rapid decrease in the electrical conductivity and in the thermoelectric power; both quantities pass through a minimum, and then rise rapidly to a maximum corresponding with Sb_2Te_3. The courses of these curves between 0 and 60 per cent. Te are typical of alloys of two crystalline phases forming solid soln. The magnetic susceptibility by H. Endo, and K. Honda and T. Sone is shown in Fig. 30. Between 100 and 62 per cent. Te, the curve is nearly a straight line, and there

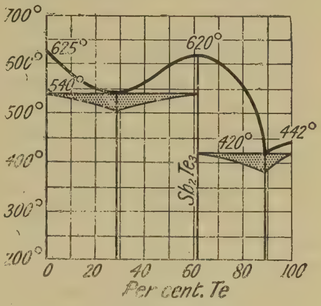


FIG. 30.—Freezing-point Curve of Mixtures of Antimony and Tellurium.

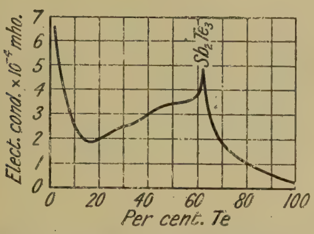


FIG. 31.—Electrical Conductivity of the Sb-Te Alloys.

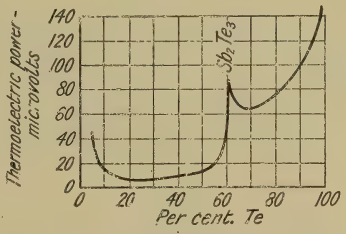


FIG. 32.—Thermoelectric Power of the Sb-Te Alloys.

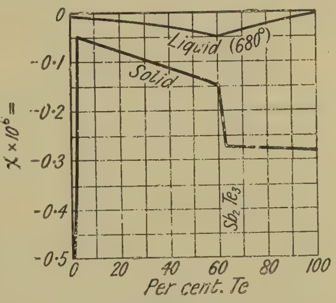


FIG. 33.—Magnetic Susceptibility of the Sb-Te Alloys.

is then a sudden change in the direction of the curve. C. H. Green studied the Sb–Te eutectic.

I. Eques a Born[20] described a mineral from Deutsch-Pilsen, Hungary, which he regarded as a compound of silver and molybdenum, and A. G. Werner called it *Molybdänsilber*. M. H. Klaproth, before his discovery of tellurium, said that it contained only sulphur and bismuth. H. Rose showed that it contains tellurium, bismuth and silver, with traces of selenium and antimony. J. J. Berzelius also showed that the mineral contains tellurium and a little selenium. A similar mineral was found at Riddarhyttan, Sweden, and J. Esmark obtained one from Telemark, Norway. A chemically different mineral was found by A. Wehrle at Schubkau, Schemnitz, and it was called **tetradymite**—from τετράδυμος, fourfold, in allusion to the twinned crystals—J. J. N. Huot called the mineral from Deutsch-Pilsen, Hungary, *wehrlite ;* but since this term had previously been applied to a variety of ilvaite—**6**. 40, 52—G. A. Kenngott proposed the term *pilsenite*. J. J. Berzelius regarded tetradymite as a compound $Bi_2S_3.2Bi_2Te_3$ (that is Bi_2STe_2). G. Rose regarded it as an isomorphous mixture of trigonal telluride and sulphide ; and C. F. Rammelsberg grouped the natural bismuth tellurides, (i) those containing selenide ; (ii) those containing sulphide—*e.g.* tetradymite ; and (iii) those containing both sulphide and selenide—*e.g.* the mineral from San José, Brazil, to which A. Damour applied the term *joséite*. J. F. L. Hausmann had previously applied the term *bornite* to a Brazilian specimen, and F. S. Beudant *bornine* to the specimen from Pilsen. The isomorphism of the bismuth sulphides, selenides, and tellurides was discussed by G. A. Kenngott, C. F. Rammelsberg, J. E. Stead, P. Groth, G. Rose, F. A. Genth, and J. D. Dana. Owing to the variable proportions of the contained tellurium, selenium, and sulphur, tetradymite has been represented by the formula $Bi_2(S,Se,Te)_3$. A. G. Werner called a variety of tetradymite, *Molybdänsilber*, and I. Eques a Born, *argent molybdique*. W. Muthmann and E. C. Schröder applied the term *grünlingite*—after F. Grünling—to a specimen from Carrock Fells, Cumberland ; and S. P. de Rubies, *oruetite* to a specimen from Serrania de Ronda, Spain.

The occurrences in Hungary were described by A. Wehrle, W. Haidinger, V. R. von Zepharovich, W. Muthmann and E. C. Schröder, L. Sipöcz, A. Frenzel, J. C. Döll, K. F. Peters, F. Posepny, and P. Partsch ; in Bohemia, by F. Slavik ; in Silesia, by M. Websky ; in England, by R. P. Greg and W. G. Lettsom, C. F. Rammelsberg, and W. Muthmann and E. C. Schröder ; in Russia, by K. Nenadkevie ; in Norway, by A. Erdmann ; in Sweden, by A. Erdmann, and J. J. Berzelius ; in Canada, by R. A. A. Johnston ; in Virginia, by H. J. Burkart, C. T. Jackson, C. Fisher, and J. D. Dana ; in North Carolina, by F. A. Genth ; in South Carolina, by J. D. Dana ; in Georgia, by H. Credner, F. A. Genth, J. D. Dana, C. T. Jackson, U. Shepard, and D. M. Balch ; in Idaho, by E. V. Shannon ; in Montana, Colorado, Georgia, and Arizona, by F. A. Genth, W. F. Hillebrand, and J. D. Dana ; in Brazil, by J. F. L. Hausmann, F. von Kobell, A. Damour, P. A. Dufrénoy, and F. A. Genth ; in Bolivia, by D. Forbes, and F. A. Genth ; and in New South Wales, by G. W. Card, and J. C. H. Mingaye.

The analyses may be roughly arranged in three groups : (i) those approximating to **bismuth sulphoditelluride,** Bi_2Te_2S, having 51 to 61 per cent. Bi ; 33 to 37 per cent. Te ; 3·6 to 5·1 per cent. S, and up to about 2 per cent. of Se, were analyzed by A. Wehrle, J. J. Berzelius, J. Hauschauer, J. Loczka, W. Muthmann and E. C. Schröder, B. Lightfoot, A. Frenzel, M. N. Short and E. P. Henderson, K. Nenadkevie, S. Koch, C. T. Jackson, F. A. Genth, R. A. A. Johnston, J. C. H. Mingaye, and E. V. Shannon—these include tetradymite, and joséite ; (ii) those occurring in Deutsch-Pilsen, and in North America ; and (iii) those bismuth tellurides which have 78 to 86 per cent. Bi ; 6 to 16 per cent. Te ; 3 to 9 per cent. S ; and up to about 1·5 per cent. Se—*e.g.* joséite, ($Bi_2Te_{3-6}S_6$), analyzed by A. Damour, F. A. Genth, and J. C. H. Mingaye, grünlingite, (Bi_4TeS_3), analyzed by C. F. Rammelsberg, and W. Muthmann and E. C. Schröder, and oruetite, (Bi_2TeS_4), analyzed by S. P. de Rubies. Those which have only a small proportion of sulphur approximate to **bismuth telluride,** Bi_2Te_3, having 50 to 59 per cent. Bi ; 46 to 49 per cent. Te ; and up to about 0·5 per cent. each of Se and S—analyzed by F. A. Genth, D. M. Balch,

W. F. Hillebrand, L. Sipöcz, and A. Wehrle, include wehrlite, pilsenite, and *tellurbismuth.*

J. J. Berzelius observed that when fused, tellurium and bismuth are miscible in all proportions. A. Gutbier, and K. Mönkemeyer formed all the alloys by fusing a mixture of the two elements in an atm. of hydrogen. K. Mönkemeyer found that the f.p. curve, Fig. 34, shows the existence of only one compound, Bi_2Te_3, which appears as a maximum at 573°; there is a eutectic at 261° with 99·08 per cent. Bi, and one at 388°, with 13·91 per cent. Bi. E. Kordes, and C. H. Green studied the Bi–Te eutectic. According to F. Körber and V. Haschimoto, thermal and X-ray analysis show that no compound other than Bi_2Te_3 is formed in the binary system Bi–Te; though there is evidence of the solubility of tellurium in this compound. C. A. Tibbals, and A. Brukl prepared a hydrated bismuth telluride, Bi_2Te_3, by treating a soln. of bismuth acetate with sodium telluride. This telluride is unaffected by hydrochloric acid or sulphuric acid in the cold, but it is decomposed by both when heated in the presence of the air. Nitric acid readily oxidizes it. When heated in hydrogen, the water is first expelled, then the telluride fuses and loses both tellurium and bismuth.

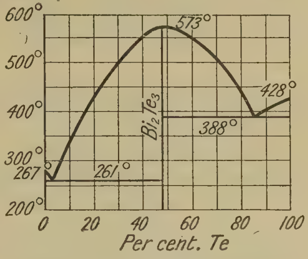


FIG. 34.—Freezing-point Curve of Bi–Te Alloys.

In his study of the tetradymites, M. Amadori investigated the f.p. of the binary system: Bi_2Te_3 and Bi_2S_3. He observed no evidence of the formation of bismuth sulphoditelluride, $2Bi_2Te_3.Bi_2S_3$, analogous to natural tetradymite; but there is a compound, $Bi_2S_3.Bi_2Te_3$—**bismuth trisulphotelluride**—which appears as a maximum at 615° on the f.p. curve, Fig. 35. It forms with bismuth telluride a eutectic at 570° containing 3 molar per cent. Bi_2S_3; and with bismuth sulphide, a eutectic approximating to the composition and f.p. of those of $Bi_2Te_3.Bi_2S_3$. No isomorphous mixtures or solid soln. of bismuth sulphide and telluride were observed, or between $Bi_2Te_3.Bi_2S_3$ and its components. M. Amadori also studied the ternary system: Bi–S–Te comprising the composition of the natural sulphotellurides, that is, Bi–Bi_2Te_3–Bi_2S_3; but no phenomena were observed which could be attributed to the formation of tetradymite, grünlingite, or joséite. The single components Bi,Bi_2S_3, and Bi_2Te_3, and the compound $Bi_2Te_3.Bi_2S_3$, separate from the fused mixtures either in the pure state, or in simple eutectic mixtures; there is no formation of new compounds, and no miscibility relationships between these substances.

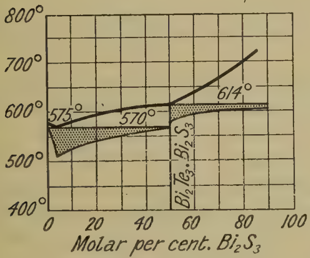


FIG. 35.—The Freezing-point Curve of the Binary System: Bi_2Te_3–Bi_2S_3.

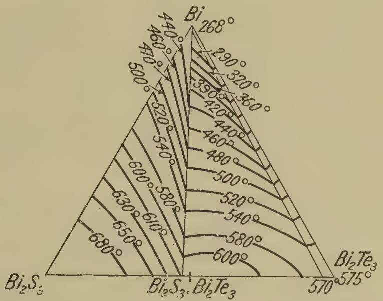


FIG. 36.—Freezing-point Curve in the Ternary System: Bi_2Te_3–Bi_2S_3–Bi.

According to A. Gutbier, the alloys with tellurium in excess are grey and brittle and show a silvery lustre when fractured; and with bismuth in excess, the alloys have a high metallic lustre and are not so brittle. Tetradymite occurs in foliated and granular masses of a steel-grey colour and metallic lustre; it also occurs in small, rarely distinct, trigonal crystals with the axial ratio, according to W. Haidinger, $a : c = 1 : 1·5871$. Twinning occurs about the $(01\bar{1}2)$-plane; and there are also fourlings. The acute trigonal crystals resemble hexagonal prisms; and the trigonal faces may be horizontally striated. The basal cleavage is perfect. The cleavage plates are flexible. W. M. Davy and C. M. Farnham, and M. N. Short and E. P. Henderson studied the etching of polished surfaces of tetradymite. The sp. gr. of the tetradymites range from 7·10 to 7·58; grünlingite, 7·32; oruetite, 7·64 to 7·94; and joséite, 7·92 to 7·94. The hardness is nearly 2. K. Mönkemeyer gave 573° for the m.p. of the artificial telluride; and L. H. Borgström, 593°–602° for the m.p. of natural tetradymite. E. Jannettaz studied the thermal conductivity. J. Joly found that when the mineral is heated, a sublimate of tellurium monoxide occurs between 460° and 480°; and of the dioxide at 750°. A. de Gramont examined the spark spectrum. W. W. Coblentz found that bismuth telluride is not photochemically sensitive. F. Beijerinck, and R. G. Harvey observed that the mineral is an electrical conductor; and W. Haken's measurements of the electrical conductivity of Bi–Te alloys are summarized in Fig. 37. The effect of the formation of the telluride is clearly shown. A. Schrauf and E. S. Dana found that tetradymite in contact with copper is thermoelectrically positive; but grünlingite, and bismuth tellurium from Georgia is negative. W. Haken's observations on the thermoelectric power of alloys of bismuth and tellurium are summarized in Fig. 38. E. Becquerel made observations on this subject. The presence of the telluride is clearly marked. E. T. Wherry said that tetradymite is a poor radio-detector. G. C. Trabacchi's observations, Fig. 39, and H. Endo's, and K. Honda and T. Sone's observations, Fig. 40, on the diamagnetic susceptibility, also show sharp singularities corresponding with the telluride. C. E. Mendenhall and W. F. Lent also made some observations on this subject.

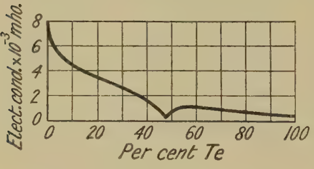


FIG. 37.—Electrical Conductivity of the Bi–Te Alloys.

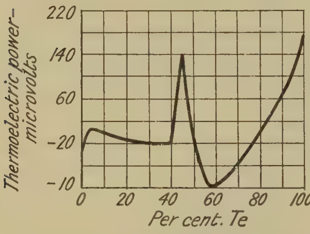


FIG. 38.—Thermoelectric Power of Bi–Te Alloys.

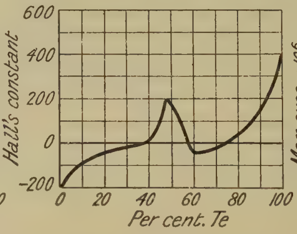


FIG. 39.—Hall's Constant with Bi–Te Alloys.

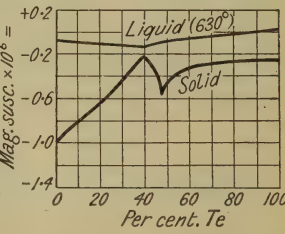


FIG. 40.—Magnetic Susceptibility of Bi–Te Alloys.

A. de Castillo[21] reported a pale steel-grey or lead-grey mineral occurring in granular masses near the Sierra de Tapalpa, Mexico; and it was called **tapalpite.** Analyses were given by C. F. Rammelsberg, and F. A. Genth; they are not very concordant; but the results agree best with the assumption that the mineral is a **silver sulphotellurobismuthite,** $Ag_3Bi(S,Te)_3$. The etching of the polished mineral was studied by W. M. Davy and C. M. Farnham. The mineral has a sp. gr. 7·803; C. F. de Landero gave 7·395. R. G. Harvey measured the electrical resistance. E. Cumenge described a fibrous mineral from the Sierra Blanca, Colorado, and it was named **vondiestite**—after M. von Diest. The analysis corresponds with **silver gold tellurobismuthite,** $(Ag,Au)_5BiTe_4$, of the same type as stephanite, Ag_5SbS_4.

I. Oftedal[22] found that the X-radiogram of **chromium telluride,** CrTe, corresponds with a lattice of the NiAs-type with $a = 2·981$A., $c = 6·211$A., and $a : c = 1 : 1·560$. According to C. A. Tibbals, when sodium telluride reacts with ammonium molybdate or sodium tungstate, dark, strongly coloured soln. are formed which are quite stable in the air. With these soln. hydrochloric acid yields black flocculent precipitates which contain tellurium and either molybdenum or tungsten, as the case may be. This is taken to mean that a **telluromolybdate,** or a **tellurotungstate** is formed. C. H. Weber recommended a trace of tellurium in tungsten incandescent filaments to make them stronger and more flexible. V. M. Goldschmidt discussed the structure of the crystals of **molybdenum ditelluride,** $MoTe_2$, and of **tungsten ditelluride,** WTe_2.

C. A. Tibbals said that **manganese telluride** is formed when sodium telluride acts on manganese acetate in the presence of acetic acid. The light brown precipitate which is first formed rapidly changes to a dark green. If the acetic acid be in excess or if the soln. be hot, the telluride is decomposed with the formation of hydrogen telluride which itself decomposes and deposits tellurium upon the walls of the vessel above the soln. The dark green precipitate is immediately blackened by exposure to air, and dil. acids decompose it very readily with liberation of hydrogen telluride. A. Brukl also prepared this compound. I. Oftedal prepared **manganese monotelluride,** MnTe, and obtained crystals with an X-radiogram corresponding with the NiAs-lattice having $a=4{\cdot}124$ A., $c=6{\cdot}98$ A., and $a:c=1{\cdot}624$; **manganese ditelluride,** $MnTe_2$, was also obtained with crystals having a lattice of the pyrites type with $a=6{\cdot}943$ A. V. M. Goldschmidt discussed the structure of the crystals.

J. J. Berzelius prepared **ferrous telluride,** presumably FeTe, by reducing ferrous tellurite with hydrogen; and J. Margottet, and C. Fabre prepared ferrous telluride by the direct union of the elements in an atm. of an inert gas. L. Moser and K. Ertl made ferrous telluride, as a grey, metallic mass, by passing the vapour of tellurium, under reduced press., over finely-divided iron. It is stable in air. According to G. Tammann and K. Schaarwächter, the two elements begin to react at 435°. I. Oftedal found the composition is not exactly FeTe, and that the X-radiograms correspond with hexagonal cells with $a=3{\cdot}800$ A., and $c=5{\cdot}651$ A. A. Brukl said that ferrous telluride is very sensitive to light, and is decomposed into its elements. Dil. acids furnish hydrogen telluride. J. Margottet, and C. Fabre found that ferrous telluride dissolves in hydrochloric acid with the evolution of hydrogen telluride. C. Fabre gave 15·58 Cals. for the heat of formation of the crystalline telluride. With respect to **ferric telluride,** C. A. Tibbals found that when sodium telluride acts upon a soln. of ferric chloride acidified with acetic acid, a black precipitate is formed which is composed entirely of tellurium. The iron is reduced to the ferrous condition and the soln. contains a large amount of tellurium as the tetrachloride. This is in accord with the fact established by V. Lenher that tellurium is soluble in a soln. of ferric chloride forming ferrous chloride and tellurium tetrachloride. A. Brukl also obtained with ferric salts and hydrogen telluride a precipitate of tellurium and ferrous telluride.

J. Margottet, and C. Fabre prepared **cobalt telluride,** CoTe, by the direct union of the elements in an inert atm.—say nitrogen. W. F. de Jong and H. W. V. Willems found that the X-radiogram of cobalt telluride agrees with a hexagonal lattice having $a=3{\cdot}89$ A., and $c=5{\cdot}36$ A.; and sp. gr. 8·85; I. Oftedal gave $a=3{\cdot}886$ A., $c=5{\cdot}360$ A., and $a:c=1:1{\cdot}380$. J. Margottet, and C. Fabre describe cobalt telluride as a grey, crystalline mass of a metallic lustre; it is not attacked by hydrochloric or sulphuric acid; it changes slowly in moist air; it is oxidized by bromine or bromine water forming cobaltous bromide, hydrobromic acid, and tellurous acid. The heat of formation is 15·30 Cals. C. A. Tibbals observed that when sodium telluride soln. acts upon soln. of cobalt acetate acidulated with acetic acid, a heavy black precipitate is formed which upon analysis shows the composition of **tetrahydrated cobalt hemitritelluride,** $Co_2Te_3, 4H_2O$, corresponding with the sodium telluride, Na_4Te_3. Acids other than nitric have no action upon it in the cold. When heated in an atm. of hydrogen, $Co_2Te_3.4H_2O$, loses water at about 200°, and at a red-heat, tellurium. If the heating is continued until the weight of substance is constant, the residue consists of the normal telluride, CoTe. A. Brukl also prepared this compound.

J. Margottet, and C. Fabre prepared **nickel monotelluride,** NiTe, by heating nickel in the vapour of tellurium; they found it to consist of small reddish crystals with properties like those of the corresponding cobalt telluride. W. F. de Jong and H. W. V. Willems found that the X-radiogram agrees with a hexagonal lattice having a=3·95 A., and c=5·36 A.; and sp. gr. 8·55. I. Oftedal gave a=3·957 A., c=5·354 A., and $a:c$=1 : 1·353. C. Fabre gave for the heat of formation 15·10 Cals.; and W. A. Tilden found the mol. ht. to be—

	100°	200°	300°	400°	500°	600°	700°
Mol. ht. . . .	8·38	11·35	12·41	12·92	13·15	13·28	13·35

According to C. A. Tibbals, sodium telluride precipitates the *tetrahydrate*, $Ni_2Te_3.4H_2O$, from acetic acid soln. of nickel acetate; it is not acted on by cold hydrochloric or sulphuric acid, but is readily oxidized by nitric acid; when heated in hydrogen it loses water and tellurium forming the monotelluride. A. Brukl also prepared this compound.

F. A. Genth[23] described a mineral from Melones Mine, Calaveras Co., California, and it was called **melonite.** W. F. Hillebrand found that it also occurs in Boulder Co., Colorado; and A. Dieseldorff, at Worturpa, South Australia. Analyses, reported by F. A. Genth, and C. F. Rammelsberg, agreed with the formula for *nickel hemitritelluride*, Ni_2Te_3; and those by W. F. Hillebrand, and A. Dieseldorff, with *nickel ditelluride*, $NiTe_2$. A. Dieseldorff gave 7·270 to 7·403 for the sp. gr.; and 1·0 to 1·5 for the hardness. The mineral is reddish-white, and generally occurs in indistinct granular and foliated particles. F. A. Genth thought that it is hexagonal with a marked basal cleavage. W. M. Davy and C. M. Farnham studied the etching of polished surfaces.

N. W. Fischer[24] found that elementary tellurium acts as a reducing agent towards soln. of platinum salts; and F. Rössler, that eq. proportions of platinum and tellurium unite explosively at elevated temp. forming **platinum ditelluride,** $PtTe_2$; and when the ditelluride is fused, **platinum monotelluride,** PtTe, crystallizes out. A. Brukl also obtained the ditelluride by the action of sodium telluride on platinum tetrachloride. According to C. A. Tibbals, a soln. of sodium telluride, acting upon a soln. containing platinum tetrachloride in excess, produces a heavy black precipitate, which is composed entirely of platinum. The tellurium is found in the soln. The reaction may be expressed by the equation, $2Na_2Te+3PtCl_4=4NaCl+2TeCl_4+3Pt$. L. Thomassen observed that platinum ditelluride has crystals of the cadmium iodide type with a space-lattice having a=4·010 A., and c=5·118 A. V. M. Goldschmidt discussed the structure of the crystals. N. W. Fischer found that tellurium acts as a reducing agent toward palladium soln. in a manner analogous to its action upon silver, gold and platinum soln. Sodium telluride precipitates from sodium palladous chloride soln. a very finely-divided black precipitate of **palladous telluride.** This substance is not acted upon by hydrochloric or sulphuric acids in the cold, but is oxidized by nitric acid and very readily dissolved by aqua regia. A. Brukl said that platinum ditelluride is soluble in soln. of sodium and ammonium tellurides, and sparingly soluble in soln. of ammonium and sodium sulphides; it is stable towards hydrochloric acid; nitric acid dissolves all the tellurium and a part of the platinum. It decomposes easily into its elements. A. Brukl obtained **palladium telluride,** PdTe, by the action of sodium telluride on a soln. of palladous chloride, hydrogen telluride reduces the salt to metal. The black telluride is not attacked by dil. acids, but nitric acid oxidizes it readily. L. Thomassen found that the crystals of the monotelluride are of the nickel arsenide type with a space-lattice having a=4·127 A., and c=5·663 A. He also prepared **palladium ditelluride,** $PdTe_2$, in crystals of the cadmium iodide type having a space-lattice with a=4·028 A., and c=5·118 A. The crystals of **ruthenium ditelluride,** $RuTe_2$, are of the pyrites type having a space-lattice with a=6·360 A., whilst a product of the composition of **ruthenium monotelluride,** RuTe, was found to be a mixture of the ditelluride and the metal. Similarly, **osmium ditelluride,** $OsTe_2$, which has crystals of the pyrite type, having the lattice parameter a=6·369 A.; and a product with the composition of **osmium monotelluride,** OsTe, is really a mixture of the ditelluride and metal. None of the compounds showed any evidence of ferromagnetism. V. M. Goldschmidt discussed the structure of these ditellurides.

REFERENCES.

[1] A. Bineau, *Ann. Chim. Phys.*, (2), **67**. 231, 1838; (2), **68**. 438, 1838; E. Wendehorst, *Zeit. anorg. Chem.*, **153**. 263, 1926; A. F. Hallimond, *Min. Mag.*, **21**. 480, 1928.

[2] H. Davy, *Phil. Trans.*, **100**. 16, 231, 1810; J. J. Berzelius, *Schweigger's Journ.*, **6**. 311, 1812; **34**. 78, 1823; *Pogg. Ann.*, **28**. 392, 1833; **32**. 1, 577, 1834; A. Oppenheim, *Journ. prakt. Chem.*, (1), **81**. 308, 1860; *Beobachtungen über das Tellur und einige seiner Verbindungen*, Göttingen, 1857; M. Berthelot and C. Fabre, *Ann. Chim. Phys.*, (6), **14**. 103, 1887; E. Ernyei, *Zeit. anorg. Chem.*, **25**. 313, 1900; C. Hugot, *Compt. Rend.*, **129**. 388, 1899; L. A. Tschugaeff and V. G. Chlopin, *Journ. Russ. Phys. Chem. Soc.*, **47**. 364, 1915; *Ber.*, **47**. 1269, 1914; C. A. Kraus and C. Y. Chiu, *Journ. Amer. Chem. Soc.*, **44**. 1999, 1922; C. A. Kraus and E. H. Zeitfuchs, *ib.*, **44**. 2714, 1922; C. A. Kraus and S. W. Glass, *Journ. Phys. Chem.*, **33**. 984, 995, 1929; E. Demarçay, *Bull. Soc. Chim.*, (2), **40**. 99, 1883; G. Magnus, *Pogg. Ann.*, **17**. 521, 1829; F. and C. Heberlein, *Berg. Hütt. Ztg.*, **54**. 43, 1895; A. Brinkmann, *Beiträge zur Kenntniss der Lithiumverbindungen*, Erlangen, 1892; G. Pellini and E. Quercigh, *Atti Accad. Lincei*, (5), **19**. ii, 350, 1910; D. M. Liddell, *Chem. Met. Engg.*, **25**. 453, 1921; C. A. Tibbals, *Journ. Amer. Chem. Soc.*, **31**. 902, 1909; *Bull. Univ. Wisconsin*, 274, 1909; *A Study of Tellurides*, Madison, Wis., 1909.

[3] J. J. Berzelius, *Schweigger's Journ.*, **6**. 311, 1912; **34**. 78, 1823; *Pogg. Ann.*, **8**. 411, 1826; **28**. 392, 1833; **32**. 1, 577, 1834; N. A. Puschin, *Journ. Russ. Phys. Chem. Soc.*, **39**. 13, 1907; *Rev. Mét.*, **4**. 929, 1907; *Zeit. anorg. Chem.*, **56**. 9, 1908; M. Chikashige, *ib.*, **54**. 50, 1907; G. Tammann, *ib.*, **118**. 93, 1921; W. C. Roberts-Austen, *Engg.*, **59**. 742, 1895; *Proc. Inst. Mech. Eng.*, 238, 1895; B. Brauner, *Journ. Russ. Phys. Chem. Soc.*, **15**. 433, 1883; *Journ. Chem. Soc.* **55**. 382, 1889; *Monatsh.*, **9**. 423, 1889; *Sitzber. Akad. Wien*, **98**. 456, 1889; *Journ. Russ. Phys. Chem. Soc.*, **15**. 433, 1883; *Ber.*, **16**. 3055, 1883; B. Brauner and B. Kuzma, *ib.*, **40**. 3363, 1907; M. L. Huggins, *Phys. Rev.*, (2), **21**. 211, 1923; J. Margottet, *Recherches sur les sulfures, les séléniures, et les tellurures métalliques*, Paris, 1879; *Ann. École Norm.*, (2), **8**. 247, 1879; *Compt. Rend.*, **84**. 1293, 1877; **85**. 1142, 1877; C. Fabre, *ib.*, **105**. 277, 1887; *Ann. Chim. Phys.*, (6), **14**. 118, 1889; F. W. Hinrichsen and O. Bauer, *Mitt. Materialprüf. Amt.*, **25**. 119, 1907; E. Heyn and O. Bauer, *Met.*, **3**. 73, 1906; W. M. Davy and C. M. Farnham, *Microscopic Examination of Ore Minerals*, New York, 35, 1920; C. Whitehead, *Journ. Amer. Chem. Soc.*, **17**. 849, 1896; A. Brukl, *Rec. Trav. Chim. Pays-Bas*, **45**. 471, 1924; T. Parkman, *Amer. Journ. Science*, (2), **33**. 335, 1868; W. E. Ford, *ib.*, (4), **15**. 69, 1903; W. P. Crawford, *ib.*, (5), **13**. 345, 1927; F. Garelli, *Atti Accad. Torina*, **58**. 193, 297, 1923; P. Köthner, *Liebig's Ann.*, **319**. 1, 1901; *Das reine Tellur und sein Atomgewicht*, Halle, 1901; A. Beutell, *Centr. Min.*, 14, 1919; C. A. Tibbals, *Bull. Univ. Wisconsin*, 274, 1909; *A Study of Tellurides*, Madison, Wis., 1909; *Journ. Amer. Chem. Soc.*, **31**. 902, 1909; G. von Hevesy and W. Serth, *Zeit. anorg. Chem.*, **180**. 150, 1929; E. T. Wherry, *Amer. Min.*, **10**. 28, 1925; I. Stransky, *Zeit. phys. Chem.*, **113**. 131, 1924; A. Mazzucchelli and A. Vercillo, *Atti Accad. Lincei*, (6), **1**. 233, 1925; G. P. Thomson, *Proc. Roy. Soc.*, **128**. A, 649, 1930.

[4] A. Schrauf, *Zeit. Kryst.*, **2**. 245, 1878; A. des Cloizeaux, *Manuel de minéralogie*, Paris, 320, 1893; V. Goldschmidt, *Index der Krystallformen der Mineralien*, Berlin, **3**. 194, 1891; C. Hintze, *Handbuch der Mineralogie*, Leipzig, **1**. i, 433, 1899; E. S. Dana, *A System of Mineralogy*, New York, 46, 1892; A. Stütz, *Physikalischmineralogischen Beschreibung des Gold- und Silberbergwerks zu Szekerembe bei Nagyag*, Wien, 153, 1803; *Schrift. Nat. Ges. Wien*, 1, 1803; S. Koch, *Ban. Koh. Lapok*, **62**. 425, 449, 1929.

[5] H. Pélabon, *Ann. Chim. Phys.*, (1), **17**. 526, 1909; *Compt. Rend.*, **143**. 294, 1906; M. Chikashige and I. Saito, *Mem. Coll. Kyoto*, **1**. 361, 1916; L. Jordan, L. H. Grenall and H. K. Herschman, *Trans. Amer. Inst. Min. Met. Eng.*, **75**. 151, 1927; G. Pellini and E. Quercigh, *Atti Accad. Lincei*, (5), **19**. ii, 415, 1910; E. T. Wherry, *Amer. Min.*, **10**. 30, 1925; W. M. Bradley, *Amer. Journ. Science*, (4), **38**. 163, 1914; E. J. Dittus, *ib.*, (4), **39**. 220, 1910; W. T. Schaller, *Journ. Washington Acad.*, **4**. 497, 1914; R. G. Harvey, *Econ. Geol.*, **23**. 778, 1928.

[6] G. Rose, *Reise nach dem Ural, dem Altai, und dem kaspischen Meere*, Berlin, **1**. 520, 614, 1837; *Pogg. Ann.*, **18**. 64, 1830; W. Petz, *ib.*, **57**. 470, 1842; H. Hess, *ib.*, **28**. 408, 1833; H. Rose, *Das krystallochemischen Mineralsystem*, Leipzig, 50, 1852; K. A. Nemadkevich, *Compt. Rend. Acad. Russ.*, 139, 1924; J. Fröbel, *Grundzüge eines Systems der Krystallologie*, Leipzig, 49, 1843; W. Haidinger, *Handbuch der bestimmenden Mineralogie*, Wien, 596, 1845; J. J. N. Huot, *Manuel de minéralogie*, Paris, **1**. 187, 1848; E. F. Glocker, *Handbuch der Mineralogie*, Nürnberg, 439, 1831; G. A. Kenngott, *Uebersichte der Resultate mineralogischen Forschungen*, Wien, 135, 1854; *Sitzber. Akad. Wien*, **11**. 20, 1853; K. F. Peters, *ib.*, **44**. 110, 1861; N. von Kokscharoff, *Materialen zur Mineralogie Russlands*, St. Petersburg, **2**. 182, 1857; J. D. Dana, *A System of Mineralogy*, New York, 48, 1892; J. F. L. Hausmann, *Handbuch der Mineralogie*, Göttingen,

51, 1847; C. F. Rammelsberg, *Handwörterbuch der chemischen Theils der Mineralogie*, Berlin, 220, 1849; *Handbuch der Mineralchemie*, Leipzig, 15, 1860; P. Groth, *Die Mineraliensammlung der Universität Strassburg*, Strassburg, 52, 1878; *Tabellarische Uebersichte der Mineralien*, Braunschweig, 27, 1898; G. Küstel, *Oesterr. Zeit. Berg. Hütt*, **21**. 109, 1873; *Min. Scient. Press.*, **10**. 306, 1865; *Berg. Hütt. Ztg.*, **25**. 128, 1866; *Bull. Soc. Chim.*, (2), **20**. 174, 1873; L. J. Spencer, *Min. Mag.*, **13**. 268, 1903; A. Schrauf, *Zeit. Kryst.*, **2**. 242, 1878; J. Loczka, *ib.*, **20**. 318, 1892; J. M. Rivière, *Sur la résistance électrique de quelques mélanges de tellure et d'argent, et ses variations avec la temperature*, Paris, 1911; J. Joly, *Phil. Mag.*, (6), **27**. 1, 1914; F. W. Clarke, *Bull. U.S. Geol. Sur.*, 419, 1910; F. Becke, *Tschermak's Mitt.*, (2), **3**. 312, 1881; B. Silliman, *Proc. California Acad. Nat. Science*, **3**. 378, 1867; A. des Cloizeaux, *Manuel de minéralogie*, Paris, **2**. 312, 1893; I. Domeyko, *Elementos de mineralojia*, Santiago, 407, 1879; *Compt. Rend.*, **81**. 632, 1875; A. Carnot, *ib.*, **132**. 1298, 1901; J. B. Senderens, *ib.*, **104**. 175, 1887; L. Jordan, L. H. Grenall and H. K. Herschman, *Trans. Amer. Inst. Min. Eng.*, **75**. 151, 1927; F. J. Malaguti and J. Durocher, *Ann. Mines*, (4), **17**. 60, 1850; F. A. Genth, *Proc. Amer. Phil. Soc.*, **14**. 226, 1874; **17**. **115**. 1877; **24**. 23, 1887; *Amer. Journ. Science*, (2), **45**. 310, 1868; F. A. Genth and S. L. Penfield, *ib.*, (3), **43**. 187, 1892; W. P. Blake, *ib.*, (2), **23**. 270, 1857; G. J. Brush, *ib.*, (2), **24**. 120, 1857; C. Palache, *ib.*, (4), **10**. 422, 1900; T. L. Walker and A. L. Parsons, *Univ. Toronto Geol. Stud.*, 20, 1923; B. Brauner, *Sitzber. Akad. Wien*, **98**. 486, 1889; *Monatsh.*, **10**. 421, 1889; *Journ. Chem. Soc.*, **55**. 382, 1889; P. Krusch, *Centr. Min.*, 199, 1901; *Zeit. prakt. Geol.*, **9**. 211, 1901; T. A. Richard, *Trans. Inst. Min. Met.*, **6**. 194, 1898; *Trans. Acad. Inst. Min. Eng.*, **30**. 708, 1901; *Australian Min. Standard*, **19**. 153, 190, 1901; *Eng. Min. Journ.*, **65**. 494, 1898; W. M. Davy and C. M. Farnham, *Microscopic Examination of Ore Minerals*, New York, 66, 1920; G. Tammann, *Zeit. anorg. Chem.*, **118**. 93, 1921; E. S. Simpson, *Bull. West Australia Geol. Sur.*, 43, 1912; L. S. Ramsdell, *Amer. Min.*, **10**. 289, 1925; E. T. Wherry, *ib.*, **10**. 30, 1895; G. Suckow, *Beiträge zur Physik, Chemie, und Mineralogie*, Leipzig, 113, 1837; C. A. Tibbals, *Bull. Univ. Wisconsin*, 274, 1909; *Journ. Amer. Chem. Soc.*, **31**. 902, 1909; R. D. Hall and V. Lenher, *ib.*, **24**. 918, 1902; G. Pellini and E. Quercigh, *Atti Accad. Lincei*, (5), **19**. ii, 415, 1910; M. Chikashige and I. Saito, *Mem. Coll. Kyoto*, **1**. 361, 1916; H. Pélabon, *Ann. Chim. Phys.*, (8), **17**. 526, 1909; *Compt. Rend.*, **143**. 294, 1906; J. Margottet, *ib.*, **85**. 1142, 1877; *Recherches sur les sulfures, les séléniures, et les tellurures métalliques*, Paris, 1879; *Ann. École Norm.*, (2), **8**. 247, 1879; P. von Jeremejeff, *Proc. Russ. Min. Soc.*, **18**. 283, 1882; K. Friedrich and A. Leroux, *Met.*, **3**. 371, 1906; J. A. Krenner, *Termes. Közl.*, **11**. 380, 1879; *Zeit. Kryst*, **4**, 542, 1880; A. Brukl, *Rec. Trav. Chim. Pays-Bas*, **45**. 471, 1924; G. vom Rath, *Ber. Friederich. Ges. Bonn*, 78, 1876; M. L. Huggins, *Phys. Rev.*, (2), **21**. 218, 1923; H. E. McKinstry, *Econ. Geol.*, **22**. 669, 1927; T. L. Walker and A. L. Parsons, *Bull. Univ. Toronto Geol. Series*, 20, 1925; C. F. de Landero, *Sinopsis mineralogica a catalogo descriptivo de los minerales*, Mexico, 218, 1888; E. V. Shannon, *Journ. Washington Acad.*, **15**. 342, 1925; H. J. Burkart, *Neues Jahrb. Min.*, 485, 1873; F. von Richthofen, *Jahrb. geol. Reichsanst. Wien*, **11**. 253, 1860; F. Osmond and W. C. Roberts-Austen, *Phil. Trans.*, **187**. A, 417, 1896; *Bull. Soc. Enc. Nat. Ind.*, (5), **1**. 1136, 1896; *Contribution à l'étude des alliages*, Paris, 71, 1901; G. von Hevesy and W. Serth, *Zeit. anorg. Chem.*, **180**. 150, 1929; R. G. Harvey, *Econ. Geol.*, **23**. 778, 1928; F. Osmond, *Engg.*, **66**. 756, 1898; W. C. Roberts-Austen, *Phil. Trans.*, **179**. A, 339, 1888; T. Andrews, *Engg.*, **67**. 87, 1899; J. Arnold and J. Jefferson, *ib.*, **61**. 176, 1896; A. de Gramont, *Bull. Soc. Min.*, **18**. 349, 1895; *Analyse spectrale directe des minéraux*, Paris, 1895; F. Beijerinck, *Neues Jahrb. Min. B.B.*, **11**. 439, 1897; J. Joly, *Phil. Mag.*, (6), **25**. 856, 1913; L. S. Ramsdell, *Amer. Min.*, **10**. 281, 1925; V. Rosicky, *Bull. Acad. Bohème*, 13, 1908; R. Pilz, *Zeit. prakt. Geol.*, **22**. 373, 1914; A. Beutell, *Centr. Min.*, 14, 1919; L. Tokody, *Foldt. Kozl.*, **53**. 127, 1923; F. Henglein, *Zeit. Elektrochem.*, **30**. 5, 1924; *Zeit. anorg. Chem.*, **120**. 77, 1922; T. W. Case, *Phys. Rev.*, (2), **9**. 305, 1917; N. A. Puschin, *Journ. Russ. Phys. Chem. Soc.*, **39**. 13, 1907; *Rev. Met.*, **4**. 929, 1907; *Zeit. anorg. Chem.*, **56**. 9, 1908; A. Carnot, *Compt. Rend.*, **132**. 1298, 1901; *Bull. Soc. Min.*, **24**. 357, 1901; *Ann. Mines*, (9), **19**. 530, 1901; S. Koch, *Ban. Koh. Lapok*, **62**. 425, 449, 1929.

[7] J. A. Krenner, *Termes. Közl.*, **11**. 636, 1877; *Wied. Ann.*, **11**. 636, 1877; G. vom Rath, *Ber. Niederrh. Ges. Bonn*, 225, 1877; *Sitzber. Akad. Berlin*, 292, 1877; A. H. Chester, *Amer. Journ. Science*, (4), **5**. 375, 1898; R. Scharizer, *Jahrb. geol. Reichsanst. Wien*, **30**. 604, 1888; L. Sipöcz, *Zeit. Kryst.*, **11**. 210, 1885; A. Schrauf, *ib.*, **2**. 236, 1878; A. Gmehling, *ib.*, **33**. 203, 1900; *Bol. Soc. Min. Santiago*, (3), **10**. 135, 1898; A. Stütz, *Physikalischmineralgischen Beschreibung des Gold- und Silberbergwerks zu Szekerembe bei Nagyag*, Wien, 153, 1803; *Schrift. Nat. Ges. Wien*, 1803; J. D. Dana, *A System of Mineralogy*, New York, 104, 1892; W. M. Davy and C. M. Farnham, *Microscopic Examination of the Ore Minerals*, New York, 1920; E. S. Simpson, *Bull. West Australia Geol. Sur.*, 42, 1912; H. E. McKinstry, *Econ. Geol.*, **22**. 669, 1927; M. H. Klaproth, *Beiträge zur chemischen Kenntniss der Mineralkörpen*, Berlin, **3**. 25, 1802; W. Petz, *Pogg. Ann.*, **57**. 457, 1842; A. Frenzel, *Tschermak's Mitt.*, (2), **17**. 288, 1898; E. F. Pittman, *Rec. New South Wales Geol. Sur.*, **5**. 203, 1898; W. Phillips, *Elementary Introduction to Mineralogy*, London, 328, 1823; W. Haidinger, *Treatise on Mineralogy*, Edinburgh, **3**. 171, 1825; W. H. Miller, *Introduction to Mineralogy*, London, 637, 1852; M. Maryansky, *Zeit. prakt. Geol.*, **5**. 304, 1897; K. Schmeisser, *ib.*, **7**. 143, 1899; K. Schmeisser and K. Vogelsang, *Die Goldfelder Australasiens*, Berlin, 1897; London, 1898; H. A. Miers, *Min. Mag.*, **9**. 184, 1892; E. H. Liveing, *Eng. Min. Journ.*, **75**. 814, 1913; R. G. Harvey, *Econ. Geol.*, **23**. 778, 1928; S. Koch, *Ban. Koh. Lapok*, **62**. 425, 449, 1929.

[8] J. J. Berzelius, *Jahresb.*, **13**. 162, 1831 ; M. H. Klaproth, *Mem. Akad. Berlin*, **50**. 17, 1798 ; *Beiträge zur chemischen Kenntniss der Mineralkörpen*, Berlin, **3**. 1, 1802 ; London, **2**. 1, 1804 ; *Crell's Ann.*, **1**. 91, 1–798 ; *Gilbert's Ann.*, **12**. 246, 1802 ; A. Stütz, *Physikalischmineralogischen Beschreibung des Gold- und Silberbergwerks zu Szekerembe bei Nagyag*, Wien, 153, 1803 ; *Schrift. Nat. Ges. Wien*, 1, 1803 ; W. Petz, *Pogg. Ann.*, **57**. 476, 1842 ; F. Mohs, *Grundriss der Mineralogie*, Dresden, 327, 1823 ; C. F. Rammelsberg, *Handbuch der Mineralchemie*, Leipzig, **2**. 127, 1841 ; 10, 1895 ; G. Rose, *Das krystallochemischen Mineralsystem*, Leipzig, 56, 1852 ; *Elemente der Krystallographie*, Leipzig, 167, 1833 ; P. Groth, *Tabellarische Uebersicht der Mineralien*, Braunschweig, 80, 1874 ; G. A. Kenngott, *Sitzber. Akad. Wien*, **11**. 979, 1853 ; W. Phillips, *Elementary Introduction to Mineralogy*, London, 245, 1819 ; 327, 1823 ; W. H. Miller, *Introduction to Mineralogy*, London, 134, 1852 ; V. von Zepharovich, *Mineralogisches Lexicon für das Kaiserthum Oesterreich*, Wien, 442, 1859 ; J. F. L. Hausmann, *Handbuch der Mineralogie*, Göttingen, 48, 1847 ; W. Haidinger, *Treatise on Mineralogy*, Edinburgh, **3**. 21, 1825 ; N. V. Kokscharoff, *Bull. Acad. St. Petersburg*, (3), **6**. 537, 1865 ; *Materialien zur Mineralogie Russlands*, St. Petersburg, **10**. 191, 1891 ; A des Cloizeaux, *Manuel de minéralogie*, Paris, **2**. 315, 1893 ; W. M. Davy and C. M. Farnham, *Microscopic Examination of the Ore Minerals*, New York, 1920 ; J. C. L. Schröder van der Kolk, *Centr. Min.*, 76, 1901 ; E. T. Wherry, *Amer. Min.* **10**. 30, 1925 ; E. H. Liveing, *Eng. Min. Journ.*, **75**. 814, 1903 ; A. Schrauf, *Neues Jahrb. Min.*, 394, 1871 ; *Anz. Akad. Wien*, 70, 1872 ; *Zeit. Kryst.*, **2**. 211, 1878 ; J. A. Krenner, *Wied. Ann.*, **1**. 639, 1877 ; *Termes. Füzetek*, **1**. 636, 1877 ; B. von Cotta, *Berg. Hütt. Ztg.*, **20**. 155, 1861 ; J. D. Mathewson, *ib.*, **24**. 374, 1865 ; G. Küstel, **25**. 128, 1866 ; **25**. 128, 1866 ; *Min. Scient. Press.*, 60, 1865 ; *Bull. Soc. Chim.*, (2), **20**. 174, 1873 ; A. von Groddeck, *Die Lehre von den Lagerstatten der Erze*, Leipzig, 166, 1879 ; F. Beyschlag, *Zeit. prakt. Geol.*, **4**. 464, 1896 ; K. Vrba, *Ber. Böhm. Ges. Wiss.*, **47**. 1, 1894 ; F. von Richthofen, *Jahrb. geol. Reichsanst. Wien*, **11**. 253, 1860 ; J. Joly, *Phil. Mag.*, (6), **27**. 1, 1914 ; H. J. Burkart, *Neues Jahrb. Min.*, 484, 1873 ; B. Silliman, *Amer. Journ. Science*, (3), **8**. 25, 1874 ; W. F. Hillebrand, *ib.*, (3), **50**. 128, 426, 1895 ; W. H. Hobbs, *ib.*, (4), **7**. 357, 1899 ; C. Palache, *ib.*, (4), **10**. 422, 1900 ; F. W. Clarke, *ib.*, (3), **14**. 286, 1877 ; S. L. Penfield and W. E. Ford, *ib.*, (4), **12**. 225, 1901 ; V. Hanko, *Math. Term. Tud. Ertes*, **6**. 340, 1888 ; W. Lindgren and F. Ransome, *Prof. Paper U.S. Geol. Sur.*, 54, 1906 ; H. E. McKinstry, *Econ. Geol.*, **22**. 669, 1927 ; F. A. Genth, *Proc. Amer. Phil. Soc.*, **14**. 228, 1874 ; **17**. 117, 1877 ; *Amer. Journ. Science*, (2), **45**. 314, 1868 ; R. Pearce, *Proc. Colorado Scient. Soc.*, **5**. 11, 1896 ; J. D. Dana, *A System of Mineralogy*, New York, 104, 1892 ; E. P. Jennings, *Trans. Amer. Inst. Min. Eng.*, **6**. 507, 1877 ; G. C. Hoffman, *Rep. Canada Geol Sur.*, 101, 1890 ; F. C. Smith, *Journ. prakt. Chem.*, (2), **6**. 67, 1898 ; A. Frenzel, *Tschermak's Mitt.*, (2), **17**. 288, 1898 ; E. S. Simpson, *Bull. West Australia Geol. Sur.*, 42, 1912 ; C. Gastaldi, *Rend. Accad. Napoli*, (3), **17**. 22, 1911 ; G. T. Prior, *Min. Mag.*, **13**. 149, 1902 ; L. J. Spencer, *ib.*, **13**. 271, 1903 ; G. F. H. Smith, *ib.*, **13**. 121, 1903 ; J. C. H. Mingaye, *Rec. N.S.W. Geol. Sur.*, **6**. 1, 1898 ; R. W. E. MacIvor, *Chem. News*, **82**. 272, 1900 ; **86**. 308, 1902 ; T. K. Rose, *Journ. Chem. Soc.*, **63**. 714, 1893 ; A. Beutell, *Centr. Min.*, 14, 1919 ; G. Pellini and E. Quercigh, *Atti Accad. Lincei*, (5), **19**. ii, 445, 1910 ; H. Pélabon, *Ann. Chim. Phys.*, (8), **17**. 564, 1909 ; *Compt. Rend.*, **148**. 1176, 1909 ; M. Coste, *ib.*, **152**. 860, 1911 ; A. Carnot, *Compt. Rend.*, **132**. 1298, 1901 ; *Bull. Soc. Min.*, **24**. 357, 1901 ; *Ann. Mines*, (9), **19**. 530, 1901 ; P. Krusch, *Centr. Min.*, 199, 1901 ; *Zeit. prakt. Geol.*, **9**. 211, 1901 ; A. G. Holroyd, *Trans. Australian Inst. Min. Eng.*, **4**. 186, 1897 ; M. L. Huggins, *Phys. Rev.*, (2), **21**. 211, 1923 ; L. Sipöcz, *Zeit. Kryst.*, **11**. 210, 1885 ; R. G. Harvey, *Econ. Geol.*, **23**. 778, 1928 ; S. Koch, *Ban. Koh. Lapok*, **62**. 425, 449, 1929.

[9] B. Brauner, *Journ. Chem. Soc.*, **55**. 391, 1889 ; V. Lenher, *Journ. Amer. Chem. Soc.*, **24**. 355, 1902 ; C. A. Tibbals, *ib.*, **31**. 902, 1909 ; *A Study of Tellurides*, Madison, Wis., 1909 ; *Bull. Univ. Wisconsin*, 274, 1909 ; J. Margottet, *Ann. École Norm.*, (2), **8**. 283, 1879 ; *Recherches sur les sulfures, les séléniures et les tellurures métalliques*, Paris, 1879 ; *Compt. Rend.*, **84**. 1293, 1877 ; **85**. 1142, 1877 ; **105**. 1294, 1887 ; A. Brukl, *Rec. Trav. Chim. Pays-Bas*, **25**. 271, 1924 ; J. Joly, *Phil. Mag.*, (6), **27**. 1, 1914 ; W. Haidinger, *Handbuch der bestimmenden Mineralogie*, Wien, 556, 1845 ; J. F. L. Hausmann, *Handbuch der Mineralogie*, Göttingen, **2**. 51, 1847 ; W. Petz, *Pogg. Ann.*, **57**. 470, 1842 ; F. Zambonini, *Zeit. Kryst.*, **49**. 246, 1911 ; A. Schrauf, *ib.*, **2**. 326, 1878 ; R. Scharizer, *Jahresb. geol. Reichsanst. Wien*, **30**. 604, 1880 ; C. Gastaldi, *Rend. Accad. Napoli*, (2), **17**. 24, 1911 ; L. Nowack, *Zeit. Metallkunde*, **19**. 238, 1927 ; E. T. Wherry, *Amer. Min.*, **10**. 30, 1925 ; L. J. Spencer, *Min. Mag.*, **13**. 271, 1903 ; H. E. McKinstry, *Econ. Geol.*, **22**. 669, 1927 ; S. Koch, *Ban. Koh. Lapok*, **62**. 425, 449, 1929 ; A. D. Alvir, *Philippine Journ. Science*, **41**. 137, 1930.

[10] L. Pauling, *Journ. Amer. Chem. Soc.*, **49**. 765, 1927 ; M. Berthelot and C. Fabre, *Ann. Chim. Phys.*, (6), **14**. 104, 1888 ; L. Moser and K. Erth, *Zeit. anorg. Chem.*, **118**. 269, 1921 ; F. A. Henglein and R. Roth, *ib.*, **126**. 227, 1923 ; W. Zachariasen, *Zeit. phys. Chem.*, **124**. 436, 1927 ; **128**. 417, 1927 ; I. Oftedal, *ib.*, **128**. 154, 1927 ; F. Wöhler, *Pogg. Ann.*, **11**. 161, 1827 ; A. Hilger, *Zeit. anal. Chem.*, **13**. 133, 1874 ; K. Spangenberg, *Naturwiss.*, **15**. 266, 1927 ; V. M. Goldschmidt, *Vid. Akad. Skr. Oslo*, **1**. 8, 1926 ; *Zeit. Kryst.*, **69**. 411, 1929 ; M. Haase, *ib.*, **65**. 510, 1927 ; K. B. Heberlein, *Beiträge zur Kenntniss des Tellurs*, Basel, 1898 ; *Berg. Hütt. Ztg.*, **54**. 41, 1895 ; D. M. Liddell, *Chem. Met. Engg.*, **25**. 102, 268, 683, 1921.

[11] H. St. C. Deville and L. Troost, *Compt. Rend.*, **52**. 920, 1861 ; J. Margottet, *Ann. École Norm.*, (2), **8**. 283, 1879 ; *Recherches sur les sulfures, les séléniures et les tellurures métalliques*, Paris, 1879 ; *Compt. Rend.*, **84**. 1293, 1877 ; **85**. 1142, 1877 ; **105**. 1294, 1887 ; C. Fabre, *ib.*, **105**. 277, 1887 ; *Ann. Chim. Phys.*, (6), **14**. 118, 1889 ; W. Zachariasen, *Norsk. Geol. Tids.*, **8**. 302,

1926 ; *Zeit. phys. Chem.*, **124**. 277, 436, 1926 ; J. J. Berzelius, *Schweigger's Journ.*, **6**. 311, 1812 ; **34**. 78, 1823 ; *Pogg. Ann.*, **28**. 392, 1833 ; **32**. 1, 577, 1834 ; M. Kobayashi, *Zeit. anorg. Chem.*, **69**. 1, 1910 ; *Internat. Zeit. Metallog.*, **2**. 65, 1912 ; L. Moser and K. Erth, *Zeit. anorg. Chem.*, **118**. 269, 1921 ; E Kordes, *ib.*, **154**. 91, 1926 ; F. Henglein, *ib.*, **120**. 77, 1922 ; *Zeit. Elektrochem.*, **30**. 5, 1924 ; M. L. Huggins, *Phys. Rev.*, (2), **21**. 211, 1923 ; C. A; Tibbals, *Bull. Univ. Wisconsin*, 274, 1909 ; *Journ. Amer. Chem. Soc.*, **31**. 902, 1909 ; *A Study of Tellurides*, Madison, Wis., 1909 ; A. Oppenheim, *Journ. prakt. Chem.*, (1), **71**. 266, 1857 ; *Beobachtungen über des Tellur und einige seiner Verbindungen*, Göttingen, 1857 ; W. Hartvig, *Sitzber. Akad. Berlin*, 79, 1926 ; A. Brukl, *Rec. Trav. Chim. Pays-Bas*, **45**. 471, 1924.

[12] F. A. Genth, *Proc. Amer. Phil. Soc.*, **16**. 14, 1876 ; **17**. 115, 1877 ; W. F. Hillebrand, *Amer. Journ. Science*, (4), **8**. 297, 1899 ; W. M. Davy and C. M. Farnham, *Microscopic Examination of Ore Minerals*, New York, 97, 1920 ; C. F. Rammelsberg, *Handbuch der Mineralchemie*, Leipzig, **2**. 12, 1895 ; G. A. Kenngott, *Uebersichte der Resultäte mineralogischer Forschungen*, 145, 1854 ; L. Rivot, *Ann. Mines*. (5), **6**. 556, 1854 ; A. Carnot, *ib.*, (9), **19**. 530, 1901 ; *Bull. Soc. Min.*, **24**. 357, 1901 ; *Compt. Rend.*, **132**. 1298, 1901 ; J. Margottet, *Ann. École Norm.*, (2), **8**. 283, 1879 ; *Recherches sur les sulfures, les séléniures et les tellurures méalliques*, Paris, 1879 ; *Compt. Rend.*, **84**. 1293, 1877 ; **85**. 1142, 1877 ; **105**. 1294, 1887 ; M. H. Klaproth, *Mem. Akad. Berlin*, **50**. 17, 1798 ; *Beiträge zur chemischen Kenntniss der Mineralkörpen*, Berlin, **3**. 1, 1802 ; London, **2**. 1, 1804 ; *Crell's Ann.*, **1**. 91, 1798 ; *Gilbert's Ann.*, **12**. 246, 1802 ; J. J. Berzelius, *Schweigger's Journ.*, **6**. 311, 1812 ; **34**. 78, 1823 ; *Pogg. Ann.*, **28**. 392, 1833 ; **32**. 1, 577, 1834 ; F. Beijerinck, *Neues Jahrb. Min. B.B.*, **11**. 441, 1897 ; A. C. Vournasos, *Ber.*, **44**. 3269, 1911 ; F. Krafft and R. E. Lyons, *ib.*, **27**. 1768, 1894 ; C. A. Tibbals, *Bull. Univ. Wisconsin*, 274, 1909 ; *A Study of Tellurides*, Madison, Wis., 1909 ; *Journ. Amer. Chem. Soc.*, **31**. 919, 1909 ; L. J. Spencer, *Min. Mag.*, **13**. 274, 1903 ; E. S. Simpson, 57, 1899 ; 6, 1902 ; *Bull. West Australia Geol. Sur.*, 4, 1900 ; *Ann. Rep. West Australia Geol. Sur.*, **44**. 1898 ; E. F. Pittmann, *Rec. N.S.W. Geol. Sur.*, **5**. 202, 1898 ; **6**. 1, 1898 ; *Australian Min. Standard*, **13**. 2638, 2669, 2674, 1898 ; G. Pellini and C. Aureggi, *Atti Accad. Lincei*, (5), **18**. ii, 215, 1909 ; *Gazz. Chim. Ital.*, **40**. ii, 42, 1910 ; E. T. Wherry, *Amer. Min.*, **10**. 30, 1925 ; E. H. Liveing, *Eng. Min. Journ.*, **75**. 814, 1903 ; T. A. Richard, *ib.*, **65**. 494, 1898 ; *Australian Min. Standard*, **19**. 153, 190, 1901 ; *Trans. Inst. Min. Met.*, **6**. 194, 1898 ; *Trans. Amer. Inst. Min. Eng.*, **30**. 708, 1901 ; F. de Jong, *Zeit. Kryst.*, **63**. 466, 1926 ; W. Zachariasen, *Norsk. Geol. Tids.*, **8**. 302, 1926 ; *Zeit. phys. Chem.*, **124**. 277, 436, 1926 ; F. Henglein, *Zeit. Elektrochem.*, **30**. 5, 1924 ; *Zeit. anorg. Chem.*, **120**. 77, 1922 ; M. L. Huggins, *Phys. Rev.*, (2), **21**. 211, 1923 ; J. Joly, *Phil. Mag.*, (6), **27**. 1, 1914 ; H. E. McKinstry, *Econ. Geol.*, **22**. 669, 1927 ; R. G. Harvey, *Econ. Geol.*, **23**. 778, 1928 ; A. Brukl, *Rec. Trav. Chim. Pays-Bas*, **45**. 471, 1924 ; P. I. Wolf and J. M. Hyatt, *Phys. Rev.*, (2), **36**. 375, 1930.

[13] F. Wöhler, *Pogg. Ann.*, **11**. 161, 1827 ; C. Whitehead, *Journ. Amer. Chem. Soc.*, **17**. 849, 1895 ; L. Moser and K. Erth, *Zeit. anorg. Chem.*, **118**. 269, 1921 ; D. M. Liddel, *Chem. Met. Engg.*, **25**. 102, 268, 453, 1921 ; R. de Forcrand and H. Fonzes-Diacon, *Compt. Rend.*, **134**. 1209, 1902 ; H. Moissan, *ib.*, **114**. 617, 1892 ; M. Chikashige and J. Nosé, *Mem. Coll. Kyoto*, **2**. 227, 1917 ; F. T. Sisco and M. R. Whitmore, *Journ. Ind. Eng. Chem.*, **16**. 828, 1924 ; A. L. Pocock, C. T. Calver and W. H. Walkins, *Brit. Pat. No.* 234547, 1924 ; G. Natta, *Giorn. Chim. Ind. Appl.*, **8**. 367, 1926.

[14] C. Renz, *Ber.*, **37**. 2112, 1904 ; H. Pélabon, *Ann. Chim. Phys.*, (8), **17**. 526, 1909 ; *Compt. Rend.*, **145**. 118, 1907 ; C. Fabre, *ib.*, **105**. 277, 1887 ; *Ann. Chim. Phys.*, (6), 14. 118, 1889 ; A. Brukl, *Rec. Trav. Chim. Pays-Bas*. **45**. 471, 1924 ; M. Chikashige, *Zeit. anorg. Chem.*, **78**. 68, 1912 ; G. Tammann, *ib.*, **118**. 93, 1921.

[15] J. J. Berzelius, *Schweigger's Journ.*, **6**. 311, 1812 ; **34**. 78, 1823 ; *Pogg. Ann.*, **28**. 392, 1833 ; **32**. 1, 577, 1834 ; K. Honda and T. Sone, *Journ. Inst. Metals*, **37**. 29, 1927 ; *Science Rep. Univ. Tokyo*, **2**. 10, 1913 ; H. Endo, *ib.*, **16**. 201, 1927 ; W. Biltz and W. Mecklenberg, *Zeit. anorg. Chem.*, **64**. 233, 1909 ; W. Hess, *ib.*, **163**. 220, 1927 ; A. Stock and P. Praetorius, *Ber.*, **47**. 131, 1914 ; A. Stock and H. Blumenthal, *ib.*, **44**. 1832, 1911 ; M. Kobayashi, *Mem. Coll. Eng. Kyoto*, **2**. 353, 1910 ; *Zeit. anorg. Chem.*, **69**. 1, 1910 ; E. Kordes, *ib.*, **154**. 91, 1926 ; **69**. 8, 1911 ; G. Tammann, *ib.*, **118**. 93, 1921 ; N. A. Puschin, *ib.*, **56**. 15, 1908 ; *Journ. Russ. Phys. Chem. Soc.*, **39**. 13, 1906 ; A. Brukl, *Rec. Trav. Chim. Pays-Bas*, **45**. 271, 1924 ; D. M. Liddell, *Chem. Met. Engg.*, **25**. 102, 268, 454, 1921 ; G. Natta, *Gazz. Chim. Ital.*, **58**. 344, 1928 ; V. M. Goldschmidt, *Trans. Faraday Soc.*, **25**. 253, 1929 ; A. Ditte, *Ann. Chim. Phys.*, (8), **12**. 255, 1907 ; *Compt. Rend.*, **96**. 1792, 1883 ; **97**. 42, 1883 ; H. Pélabon, *ib.*, **142**. 1149, 1906 ; *Ann. Chim. Phys.*, (8), **17**. 526, 1909 ; C. Fabre, *ib.*, (6), **14**. 168, 1889 ; *Compt. Rend.*, **105**. 227, 1887 ; A. W. Smith, *Journ. Franklin Inst.*, **192**. 69, 157, 1921 ; *Thermal, Electrical and Magnetic Properties of Alloys*, Columbus, 1921 ; H. Fay, *Journ. Amer. Chem. Soc.*, **29**. 1265, 1907 ; I. Oftedal, *Zeit. Phys. Chem.*, **134**. 301, 1928 ; W. Haken, *Ann. Physik*, (4), **32**. 298, 1910.

[16] K. Honda and T. Sone, *Journ. Inst. Metals*, **37**. 29, 1927 ; *Science Rep. Univ. Tokyo*, **2**. 10, 1913 ; H. Endo, *ib.*, **16**. 201, 1927 ; J. J. Berzelius, *Schweigger's Journ.*, **6**. 311, 1812 ; **34**. 78, 1823 ; *Pogg. Ann.*, **28**. 392, 1833 ; **32**. 1, 577, 1834 ; H. Fay and C. B. Gillson, *Trans. Amer. Inst. Min. Eng.*, **31**. 527, 1901 ; *Amer. Chem. Journ.*, **27** 88, 1902 ; H. Pélabon, *Ann. Chim. Phys.*, (8), **17**. 557, 1909 ; C. Fabre, *ib.*, (6), **14**. 119, 1888 ; *Compt. Rend.*, **105**. 280, 1887 ; A. Mazzucchelli and A. Vercillo, *Atti Accad. Lincei*, (6), **1**. 233, 1925 ; D. M. Liddell, *Chem. Met. Engg.*, **25**. 102, 268, 453, 1921 ; M. Dreifuss, *Zeit. Elektrochem.*, **28**. 100, 1922 ; P. Günther, *ib.*, **23**. 199, 1917 ; J. Joly, *Phil. Mag.*, (6), **27**. 1, 1914 ; N. A. Puschin, *Journ. Russ. Phys. Chem. Soc.*, **39**. 13,

1907; *Zeit. anorg. Chem.*, **56**. 12, 1908; A. Brukl, *Rec. Trav. Chim. Pays-Bas*, **45**. 471, 1924; J. Margottet, *Recherches sur les sulfures, les séléniures, et les tellurures métalliques*, Paris, 1879; *Ann. École Norm.*, (2), **8**. 247, 1879; *Compt. Rend.*, **84**. 1293, 1877; **85**. 1142, 1877; C. Fabre, *ib.*, **105**. 277, 1887; *Ann. Chim. Phys.*, (6), **14**. 118, 1889; W. Haken, *Ann. Physik*, (4), **32**. 298, 1910; M. Kimura, *Mem. Coll. Kyoto*, **8**. 149, 1915; G. Rose, *Pogg. Ann.*, **18**. 68, 1830; *Reise nach dem Ural, dem Altai, und dem kaspachen Meere*, Berlin, **1**. 617, 1837; C. A. Stetefeldt, *Berg. Hütt. Ztg.*, **24**. 374, 1865; W. Haidinger, *Handbuch der bestimmenden Mineralogie*, Wien, 556, 1845; I. Domeyko, *Compt. Rend.*, **81**. 632, 1875; *Elementos de mineralojia*, Santiago, 336, 407, 1879; J. J. N. Huot, *Manuel de minéralogie*, Paris, **1**. 185, 1841; F. S. Beudant, *Traité élémentaire de minéralogie*, **2**. 539, 1832; F. M. Endlich, *Eng. Min. Journ.*, **18**. 133, 1874; A. des Cloizeaux, *Manuel de minéralogie*, Paris, **2**. 306, 1893; O. Mügge, *Centr. Min.*, 53, 1920; W. M. Davy and C. M. Farnham, *Microscopic Examination of the Ore Minerals*, New York, 43, 1920; T. W. Case, *Phys. Rev.*, (2), **9**. 305, 1917; P. Saldau, *Ann. St. Petersburg Inst. Mines*, **4**. 228, 1913; F. Henglein, *Zeit. Elektrochem.*, **30**. 5, 1924; *Zeit. anorg. Chem.*, **120**. 77, 1922; H. Endo, *Science Rep. Univ. Tokyo*, **14**. 479, 1925; **16**. 201, 1927; C. H. Green, *Trans. Amer. Inst. Min. Met. Engg.*, **71**. 651, 1925; E. Kordes, *Zeit. anorg. Chem.*, **154**. 91, 1926; G. Tammann, *ib.*, **118**. 93, 1921; F. A. Genth, *Proc. Amer. Phil. Soc.*, **14**. 225, 1874; *Amer. Journ. Science*, (2), **45**. 306, 1868; K. B. Rogers, *Chem. News*, **138**. 147, 1929; C. A. Tibbals, *Journ. Amer. Chem. Soc.*, **31**. 909, 1909; L. Pauling, *ib.*, **49**. 765, 1927; H. Louis, *Min. Mag.*, **11**. 215, 1897; L. J. Spencer, *ib.*, **13**. 274, 1903; G. C. Hoffmann, *Rep. Geol. Sur. Canada*, **6**. 29, 1893; **8**. 11, 1895; W. T. Schaller, *Bull. Univ. California*, **2**. 324, 1901; E. S. Simpson, *Bull. West Australia Geol. Sur.*, 42, 1912; L. S. Ramsdell, *Amer. Min.*, **10**. 281, 1925; E. T. Wherry, *ib.*, **10**. 30, 1925; A. C. Vournasos, *Ber.* **44**. 3269, 1911; R. G. Harvey, *Econ. Geol.*, **23**. 778, 1928.

[17] R. Metzner, *Sur quelques composés du selenium et du tellure*, Paris, 1898; *Ann. Chim. Phys.*, (7), **15**. 203, 1898; M. Damiens, *ib.*, (9), **19**. 44, 1923; W. Strecker and W. Ebert, *Ber.*, **58**. B, 2527, 1925.

[18] A. Oppenheim, *Beobachtungen über das Tellur und einige seiner Verbindungen*, Göttingen, 1859; *Journ. prakt. Chem.*, (1) **71**. 278, 1857.

[19] A. Oppenheim, *Beobachtungen über das Tellur und einige seiner Verbindungen*, Göttingen, 1859; *Journ. prakt. Chem.*, (1), **71**. 278, 1857; E. Szarvasy and C. Messinger, *Journ. Chem. Soc.*, **75**. 597, 1899; H. Pélabon, *Compt. Rend.*, **142**. 207, 1906; **146**. 1397, 1908; *Ann. Chim. Phys.*, (8), **17**. 526, 1909; E. Becquerel, *ib.*, (4), **8**. 589, 1866; H. Fay and H. E. Ashley, *Amer. Chem. Journ.*, **27**. 95, 1906; Y. Kimata, *Mem. Coll. Kyoto*, **1**. 115, 1915; W. Haken, *Ann. Physik*, (4), **32**. 291, 1910; H. Honda and T. Sone, *Journ. Inst. Metals*, **37**. 29, 1927; *Science Rep. Univ. Tokyo*, **2**. 9, 1913; H. Endo, *ib.*, **16**. 201, 1927; C. A. Tibbals, *Journ. Amer. Chem. Soc.*, **31**. 919, 1909; *Bull. Univ. Wisconsin*, 274, 1909; *A Study of Telluride*, Madison, Wis., 1909; M. Dreifuss, *Zeit. Elektrochem.*, **28**. 100, 1921; N. S. Konstantinoff and V. I. Smirnoff, *Ann. Inst. Polyt. Petrograd*, **23**. 713, 1915; A. Brukl, *Rec. Trav. Chim. Pays-Bas*, **45**. 271, 1924; C. H. Green, *Trans. Amer. Inst. Min. Met. Eng.*, **71**. 651, 1925; M. Padoa, *Gazz. Chim. Ital.*, **57**. 399, 1927.

[20] I. Eques a Born, *Catalogue méthodique et raisonné de la collection des fossiles de Mlle. Eleonore de Raab*, Wien, **2**. 419, 1790; M. H. Klaproth, *Beiträge zur chemischen Kenntniss der Mineralkörper*, Berlin, **1**. 253, 1795; J. J. Berzelius, *Akad. Handl. Stockholm*, 183, 1823; *Pogg. Ann.*, **1**. 271, 1824; *Edin. Journ. Science*, **3**. 327, 1825; *Jahresb.*, **12** 178, 1831; H. Rose, *Gilbert's Ann.*, **72**. 196, 1822; G. Rose, *Sitzber. Akad. Berlin*, 93, 1849; *Pogg. Ann.*, **83**. 127, 1851; J. Esmark, *Trans. Geol. Soc.*, **3**. 413, 1815; F. S. Beudant, *Traité élémentaire de minéralogie*, Paris, **2**. 538, 1832; C. F. Rammelsberg, *Handbuch der Mineralchemie*, Leipzig, 4, 1860; 4, 1895; G. A. Kenngott, *Das Mohs'che Mineralsystem*, Wien, 121, 1853; *Uebersichte der Resultate mineralogischer Forschungen*, Wien, 111, 1855; P. Groth, *Tabellarische Uebersicht der Mineralien*, Braunschweig, 18, 1898; W. Haidinger, *Pogg. Ann.*, **21**. 597, 1831; *Zeit. Phys. Math.*, **9**. 129, 1831; A. Wehrle, *ib.*, **9**. 133, 144, 1831; *Schweigger's Journ.*, **59**. 482, 1830; *Pogg. Ann.*, **21**. 599, 1831; P. Partsch, *ib.*, **21**. 595, 1831; *Zeit. phys. Math.*, **9**. 94, 1831; J. J. N. Huot, *Manuel de minéralogie*, Paris, **1**. 188, 1841; F. A. Genth, *Amer. Journ. Science*, (2), **16**. 81, 1853; (2), **19**. 16, 1855; (2), **27**. 267, 1859; (2), **31**. 368, 1861; (2), **45**. 317, 1868; (3), **40**. 114, 1890; *Proc. Amer. Phil. Soc.*, **14**. 224, 1874; **23**. 31, 1880; **23**. 30, 1885; *Amer. Mining Mag.*, **1**. 358, 1859; **2**. 64, 1860; *The Minerals of North Carolina*, Washington, 22, 1891; C. T. Jackson, *Amer. Journ. Science*, (2), **6**. 188, 1848; (2), **10**. 78, 1850; (1), **27**. 366, 1859; D. M. Balch, *ib.*, (2), **35**. 99, 1863; C. Fisher, *ib.*, (2), **7**. 282, 1849; U. Shepard, *ib.*, (2), **28**. 142, 1859; J. Hauschauer, *Journ. prakt. Chem.*, (1), **45**. 456, 1848; E. C. Schröder, *Zur Kenntnis der Verbindungen des Selens und des Tellurs*, Fürth, 1898; W. Muthmann and E. C. Schröder, *Zeit. Kryst.*, **29**. 142, 1897; J. Loczka, *ib.*, **20**. 319, 1892; *Ber. Ungarn Akad.*, **8**. 99, 1890; L. Sipöcz, *Ber.*, **19**. 98, 1886; *Zeit. Kryst.*, **11**. 212, 1885; *Tschermak's Mitt.*, (2), **7**. 271, 1886; J. C. Döll, *ib.*, (1), **4**. 91, 1874; A. Frenzel, *ib.*, (1), **3**. 293, 1873; *Neues Jahrb. Min.*, 799, 1873; H. Credner, *ib.*, 443, 1867; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, 262, 1905; J. D. Dana, *A System of Mineralogy*, New York, 40, 1892; F. Beijerinck, *Neues Jahrb Min. B.B.*, **11**. 422, 1897; E. Jannettaz, *Bull. Soc. Min.*, **15**. 136, 1892; A. de Gramont, *ib.*, **18**. 352, 1895; *Analyse spectrale directe des minéraux*, Paris, 1895; M. Websky, *Zeit. deut. geol. Ges.*, **11**. 391, 1859; D. Forbes, *Phil. Mag.*, (4), **29**. 4, 1865; A. Schrauf and E. S. Dana, *Amer. Journ. Science*, (3), **8**. 262, 1874; *Sitzber. Akad. Wien*, **69**. 151, 1874; K. F. Peters, *ib.*, **44**. 105, 1861; F. von Kobell, *Journ. prakt. Chem.*, (1), **8**. 341, 1836; *Sitzber. München Akad.*, **1**. 167, 1871; *Neues Jahrb. Min.*, 939, 1871; H. J. Burkart, *ib.*, 476, 1873;

J. F. L. Hausmann, *ib.*, 698, 1852; C. F. Rammelsberg, *Sitzber. Akad. Berlin*, 188, 1863; V. R. von Zepharovich, *Mineralogisches Lexicon für das Kaiserthum Oesterreich*, Wien, 444, 1859; 247, 1893; F. Posepny, *Jahresb. geol. Reichsanst. Wien*, **18**. 301, 1868; R. P. Greg and W. G. Lettsom, *Manual of the Mineralogy of Great Britain and Ireland*, London, 381, 1858; A. Erdmann, *Läobok i Mineralogien*, Stockholm, 189, 1853; P. A. Dufrénoy, *Traité de minéralogie*, Paris, **2**. 631, 1845; G. W. Card, *Rec. N.S.W. Geol. Sur.*, **5**. 6, 1896; J. C. H. Mingaye, *ib.*, **1**. 25, 1903; **9**. 127, 1916; A. Damour, *Ann. Chim. Phys.*, (3), **13**. 372, 1845; E. Becquerel, *ib.*, (4), **8**. 389, 1866; J. M. Davy and C. M. Farnham, *Microscopic Examination of Ore Minerals*, New York, 61, 1920; B. Lightfoot, *Trans. Geol. Soc. South Africa*, **30**. 1, 1928; E. S. Simpson, *Bull. West Australia Geol. Sur.*, 42, 1912; A. G. Werner, *Letztes Mineralsystem*, Freiberg, 48, 1817; S. P. de Rubies, *Anal. Fis. Quim.*, **17**. 83, 1919; **18**. 335, 1920; S. P. de Rubies and F. G. Esteban, *ib.*, **19**. 347, 1921; K. Nenadkevie, *Trav. Mus. Geol. St. Petersburg*, **1**. 81, 1907; R. A. A. Johnston, *Rep. Canada Geol. Sur.*, **8**. 10, 1895; K. Mönkemeyer, *Zeit. anorg. Chem.*, **46**. 415, 1905; J. W. Retgers, *ib.*, **3**. 349, 1893; **12**. 103, 1896; *Zeit. Phys. Chem.*, **9**. 399, 1892; **12**. 593, 1893; **16**. 611, 1895; E. V. Shannon, *Amer. Min.*, **10**. 198, 1925; M. N. Short and E. P. Henderson, *ib.*, **11**. 316, 1926; E. T. Wherry, *ib.*, **10**. 30, 1925; L. H. Borgström, *Oefvers. Finska Förh.*, **57**. 24, 1915; M. Amadori, *Atti Accad. Lincei*, (5), **24**. ii, 200, 1915; (5), **27**. i, 131, 1918; W. Haken, *Ann. Physik*, (4), **32**. 291, 1910; *Ber. deut. phys. Ges.*, **12**. 229, 1910; G. C. Trabacchi, *Nuovo Cimento*, (6), **9**. 95, 1915; K. Honda and T. Sone, *Journ. Inst. Metals*, **37**. 29, 1927; *Science Rep. Univ. Tokyo*, **2**. 12, 1913; H. Endo, *ib.*, **14**. 479, 1925; **16**. 201, 1927; C. E. Mendenhall and W. F. Lent, *Phys. Rev.*, (1), **32**. 406, 1911; A. Gutbier, *Zeit. anorg. Chem.*, **31**. 331, 1902; C. A. Tibbals, *Journ. Amer. Chem. Soc.*, **31**. 909, 1909; *Bull. Univ. Wisconsin*, 274, 1909; *A Study of Tellurides*, Madison, Wis., 1909; J. E. Stead, *Journ. Soc. Chem. Ind.*, **16**. 200, 1897; J. Joly, *Phil. Mag.*, (6), **27**. 1, 1914; W. W. Coblentz, *Science Paper Bur Standards*, **18**. 596, 1922; *Various Photochemical Investigations*, Washington, 296, 1922; A. Brukl, *Rec. Trav. Chim. Pays-Bas*, **45**. 471, 1924; F. Slavik, *Rozp. Ceske Akad.*, **25**. 53, 1916; *Bull. Acad. Bohème*, **22**. 100, 1918; C. H. Green, *Trans. Amer. Inst. Min. Met. Eng.*, **71**. 651, 1925; E. Kordes, *Zeit. anorg. Chem.*, **154**. 91, 1916; M. Padoa, *Gazz. Chim. Ital.*, **57**. 399, 1927; R. G. Harvey, *Econ. Geol.*, **23**. 778, 1928; F. Körber and U. Haschimoto, *Zeit. anorg. Chem.*, **188**. 114, 1930; S. Koch, *Ban. Koh. Lapok*, **62**. 425, 449, 1929.

[21] C. F. de Landero, *Sinopsis mineralogica a catalogo descriptivo de los minerales*, Mexico, 1889; F. A. Genth, *Proc. Amer. Phil. Soc.*, **24**. 41, 1887; A. de Castillo, *Naturaleza*, **1**. 76, 1869; C. F. Rammelsberg, *Zeit. deut. geol. Ges.*, **21**. 81, 1869; W. M. Davy and C. M. Farnham, *The Microscopic Examination of Ore Minerals*, New York, 43, 1920; E. Cumenge, *Bull. Soc. Min.*, **22**. 25, 1899; V. M. Goldschmidt, *Trans. Faraday Soc.*, **25**. 253, 1929; R. G. Harvey, *Econ. Geol.*, **23**. 778, 1928.

[22] J. Margottet, *Recherches sur les sulfures, les séléniures, et les tellurures métalliques*, Paris, 1879; *Ann. École Norm.*, (2), **8**. 247, 1879; *Compt. Rend.*, **84**. 1293, 1877; **85**. 1142, 1877; C. Fabre, *ib.*, **105**. 277, 1887; *Ann. Chim. Phys.*, (6), **14**. 118, 1889; W. F. de Jong and H. W. V. Willems, *Physica*, **7**. 74, 1927; C. H. Weber, *Brit. Pat. No.* 18808, 1909; L. Moser and K. Ertl, *Zeit. anorg. Chem.*, **118**. 269, 1921; A. Brukl, *Rec. Trav. Chim. Pays-Bas*, **45**. 471, 1924; I. Oftedal, *Zeit. phys. Chem.*, **128**. 135, 1927; **132**. 208, 1928; **139**. 291, 1928; G. Tammann and K. Schaarwächter, *Zeit. anorg. Chem.*, **167**. 401, 1927; C. A. Tibbals, *Journ. Amer. Chem. Soc.*, **31**. 909, 1909; *Bull. Univ. Wisconsin*, 274, 1909; *A Study of Tellurides*, Madison, Wis., 1909; V. Lenher, *Journ. Amer. Chem. Soc.*, **30**. 744, 1908; V. W. Meloche and W. Woodstock, *ib.*, **51**. 171, 1929; V. M. Goldschmidt, *Trans. Faraday Soc.*, **25**. 253, 1929; J. J. Berzelius, *Akad. Handl. Stockholm*, 183, 1923; *Pogg. Ann.*, **1**. 271, 1824; *Edin. Journ. Science*, **3**. 327, 1825; *Jahresb.*, **12**. 178, 1831; W. A. Tilden, *Proc. Roy. Soc.*, **73**. 226, 1904.

[23] F. A. Genth, *Amer. Journ. Science*, (2), **45**. 393, 1868; W. F. Hillebrand, (4), **8**. 295, 1891; A. Dieseldorff, *Zeit. prakt. Geol.*, **7**. 423, 1899; *Centr. Min.*, **98**. 1900; 168, 1901; C. F. Rammelsberg, *Handbuch der Mineralchemie*, 17, 1875; W. M. Davy and C. M. Farnham, *Microscopic Examination of the Ore Minerals*, New York, 1920.

[24] C. A. Tibbals, *Journ. Amer. Chem. Soc.*, **31**. 909, 1909; *Bull. Univ. Wisconsin*, 274, 1909; *A Study of Tellurides*, Madison, Wis., 1909; N. W. Fischer, *Pogg. Ann.*, **12**. 502, 1828; F. Rössler, *Zeit. anorg. Chem.*, **15**. 405, 1897; *Synthese einiger Erzmineralien und analoger Metallverbindungen durch Auflösen und Kristallisierenlassen derselben geschmolzenen Metallen*, Berlin, 1895; A. Brukl, *Rec. Trav. Chim. Pays-Bas*, **45**. 471, 1924; L. Thomassen, *Zeit. phys. Chem.*, **2**. B, 349, 1929; V. M. Goldschmidt, *Trans. Faraday Soc.*, **25**. 253, 1929.

§ 8. Tellurium Monoxide and Dioxide

J. J. Berzelius[1] attempted to prepare **tellurium monoxide,** TeO, by heating a mixture of tellurium and tellurium dioxide, and by the action of dry sodium carbonate on tellurium dichloride, but without success. E. Divers and M. Shimose said that it is produced when tellurium sulphotrioxide is heated between 180° and 230° in vacuo: $TeSO_3=TeO+SO_2$, and the product washed with a dil. soln. of sodium carbonate to separate the unchanged sulphotrioxide. W. Prandtl and

P. Borinsky, and J. J. Doolan and J. R. Partington prepared the monoxide in a similar way. A little monoxide was also found by E. Divers and M. Shimose to be produced when tellurium sulphotrioxide is decomposed with a small proportion of water; and by pouring a red soln. of tellurium in sulphuric acid into a large proportion of water. Tellurium monoxide is described as a brown, porous, friable mass, which is black tinged with brown, and when rubbed with a burnisher acquires a graphitic lustre. It is stable in dry air, but decomposes when heated in vacuo into tellurium and tellurium dioxide. It is oxidized to the dioxide in moist air, but water has no action. Cold dil. acids decompose it slowly; with hot, conc. hydrochloric acid, it forms tellurium and its dioxide. Hydrogen chloride is absorbed by the monoxide without appreciable change, but when the product is heated, it melts and gives off tellurium dichloride. Sulphur dioxide reduces it slowly to tellurium; it is not altered by liquid sulphur trioxide—even when boiling; and with conc. sulphuric acid it forms a red soln. from which tellurium sulphate crystallizes: $2TeO+3H_2SO_4=Te(SO_4)_2+TeSO_3+3H_2O$. The monoxide is quickly oxidized by nitric acid, and other oxidizing agents in acidic soln., but less easily by neutral or alkaline soln. Potassium permanganate is reduced to manganate. Cold potash-lye acts slowly, but the boiling lye decomposes the monoxide with the separation of tellurium. No compounds with the monoxide—*hypotellurites*—have been prepared, and neither basic nor acidic properties could be assigned to it. W. Damiens said that the alleged monoxide is a mixture of tellurium and tellurium dioxide.

J. J. Berzelius[2] prepared **tellurium dioxide,** TeO_2, by burning tellurium in air; and by the action of nitric acid and hot sulphuric acid on tellurium. According to D. Klein and J. Morel, pulverulent tellurium, obtained by precipitation with sulphurous acid, dissolves readily in dil. nitric acid, with the evolution of nitrogen oxides. The temp. at which soln. takes place is lower the higher the conc. of the acid; with acid of sp. gr. 1·25 the action begins at −10°, *vide supra,* tellurium. At a low temp. soln. is not complete, and a greyish, curdy residue is left, which afterwards turns white, and forms long flexible microscopic needles containing both nitric and telluric acids.

J. J. Berzelius observed that hydrated tellurium dioxide or tellurous acid is precipitated if a soln. of tellurium in cold, dil. nitric acid is poured into cold water. A. Gutbier added that the nitric acid soln. should first be neutralized with ammonium carbonate before the dilution, and the white flocculent precipitate washed with hot water until freed from ammonia. D. Klein and J. Morel observed that when the soln. of tellurium in nitric acid is diluted with water, it deposits hydrated tellurium dioxide or tellurium dioxide, a certain quantity of a basic tellurium nitrate always remaining in soln. Hydrated tellurium dioxide contaminated with half a per cent. of nitric acid is formed when the nitric acid is dil., say of sp. gr. 1·1–1·2, and the action takes place at a low temp. It is a white, curdy substance which gradually changes to a yellowish-white mass of microscopic rectangular lamellæ of tellurium dioxide. When the reaction takes place at a higher temp., or if nitric acid is used, tellurium dioxide is formed in microscopic quadratic octahedra. The nitric acid soln. spontaneously deposits octahedral crystals of tellurium dioxide, and if the nitric acid employed is somewhat dil., say of sp. gr. 1·2, and the temp. has not risen above 30° during the reaction, the precipitation of tellurium dioxide is accelerated by heat. Under these conditions, about half the tellurium dioxide remains in soln. in the form of nitrate, which crystallizes out when the liquid is conc. and cooled.

J. J. Berzelius found that if a soln. of tellurium in warm conc. nitric acid be allowed to stand for some time it deposits tellurium dioxide contaminated with about half a per cent. of nitric acid which is expelled with feeble decrepitation when gently heated. J. J. Berzelius, H. L. Wills, C. Jena, and D. Klein and J. Morel obtained the dioxide by evaporating a soln. of tellurium in nitric acid to dryness, and heating the residue to dull redness; H. Rose said that a temp. of 200° is sufficient; and B. Brauner, 400°. A. Gutbier said that the nitric acid is all expelled only at a temp. at which some tellurium dioxide is volatilized. A. Oppenheim obtained crystals of the dioxide by adding alcohol to the nitric acid soln. of tellurium. N. W. Fischer heated a soln. of tellurium in conc. sulphuric acid until it was decolorized, and obtained on cooling what he regarded as an easily soluble sulphate; and J. J. Berzelius, B. Brauner, and D. Klein and J. Morel obtained a basic sulphate from a soln. of tellurium in hot, conc. sulphuric acid; with 20 per cent. sulphuric acid, tellurium dioxide is formed. D. Klein and J. Morel observed that both the basic sulphate and the basic nitrate are decomposed into tellurium dioxide and acid when washed with hot water. J. J. Berzelius, and A. Oppenheim also obtained the dioxide by pouring a boiling soln. of tellurium tetrachloride into hot water. J. J. Berzelius, and L. Staudenmaier obtained the dioxide by heating telluric acid.

Tellurium dioxide has been analyzed by J. J. Berzelius, H. L. Wills, B. Brauner, L. Staudenmaier, A. Gutbier, and others indicated in connection with the at. wt. of tellurium. The results agree with the empirical formula TeO_2. H. Remy discussed the structure of tellurous acid, H_2TeO_3. A. Brezina said that it is probable that an earth described by J. Esmark in 1798 was native tellurium dioxide; W. Petz also described a yellowish-white earth from Faczebaja which behaved like tellurium dioxide. The mineral was called **tellurite** by J. Nicol, and *tellurium ochre* by C. F. Rammelsberg. The mineral at Zalathna, and Faczebaja, Transylvania, was described by V. von Zepharovich, J. Esmark, and J. A. Krenner; and the occurrence in Colorado, and South Dakota, by F. A. Genth, F. C. Knight, and R. Pearce. W. P. Headden described an occurrence of tellurium dioxide as a white coating on the native tellurium of the Goodhope Mine, Colorado, and also as brownish-yellow, granular masses of small crystals—thought to be tetragonal. The mineral contained 78·68 per cent. of tellurium; a trace of bismuth oxide; 0·79 per cent. of ferric oxide; and 1·04 per cent. insoluble matter.

The hydrated forms of tellurium dioxide, indicated above, are supposed to be **tellurous acid,** H_2TeO_3. J. J. Berzelius prepared the acid by fusing tellurium dioxide with an equal weight of potassium carbonate, dissolving the resulting potassium tellurite in cold water, adding a scarcely perceptible excess of nitric acid; allowing the mixture to stand for some time with frequent stirring; washing the product with ice-cold water; and drying the acid in air at 12°. A solution of tellurium dioxide in potash-lye can be treated in a similar way. The preparation of the acid was also described by R. Schumann. G. O. Oberhelman and P. E. Browning described the preparation of the acid from the residues obtained in the electrolytic refining of copper.

Tellurium dioxide forms small, colourless, octahedral **crystals**; that prepared in the wet-way dries milk-white; and that obtained by slowly cooling the molten dioxide, or by pouring the liquid from the partly solidified portion furnishes needle-like crystals which, according to D. Klein and J. Morel, are probably rhombic; or, according to K. Vrba, possibly monoclinic. A. Brezina, and D. Klein and J. Morel gave for the axial ratios of the rhombic bipyramidal crystals $a:b:c=0·4566:1:0·4693$. The crystals obtained from the nitric acid soln. are, according to D. Klein and J. Morel, tetragonal, and have the axial ratio $a:c=1:1·1076$; and they appear like octahedral, doubly refracting crystals. The crystals were also described by V. M. Goldschmidt. The X-radiogram shows that the space-lattice is of the rutile type with $a=4·79$ A., and $c=3·77$ A., so that $a:c=1:0·788$. L. Pauling discussed the lattice-structure. A. Weller showed that the dioxide is an example of a colourless solid giving a coloured vapour and liquid. The hydrated oxide, or tellurous acid, appears like an earthy powder. D. Klein gave for the **specific gravity** of tetragonal tellurium oxide 5·67 at 15° to 19°; 5·68 for that obtained by heating the nitrate below 350°; and K. Vrba, 5·90 for the tetragonal crystals. For the rhombic form prepared from the fused dioxide, D. Klein gave 5·91 at 0°, and 5·88 at 12°; A. Schafarik, 5·93 at 20°; and F. W. Clarke, 5·75 at 12·5°, and 5·784 at 14°. J. J. Berzelius, and H. Rose found that when the dioxide is heated it becomes pale-yellow, and the colour darkens as the temp. rises. It begins to fuse at a dull red-heat forming a dark yellow, transparent liquid which on exposure to air volatilizes with a slight fuming. As the mass cools it solidifies and evolves enough heat to raise the temp. to dull redness. The white, crystalline mass is translucent when slowly cooled; it readily separates to a crystalline mass which is very easily broken into crystalline fragments. Single drops solidify to a transparent glass. It volatilizes and sublimes at a higher temp. than that at which the metal sublimes; and it can be melted in a crucible without much loss. B. Brauner said that a perceptible volatilization occurs at 400° or 500°. J. J. Berzelius found that at 40°, or even at a lower temp., the hydrated dioxide is resolved into the anhydrous dioxide; hence, a turbid mixture of the hydrated dioxide and water, becomes clear at this temp. as the granules of hydrated dioxide pass into crystals of the anhydrous dioxide. W. G. Mixter gave for the **heat of formation** $(Te,O_2)=87{\cdot}1$ Cals. R. Schumann gave −64320 to 77700 cals. for the free energy of tellurium dioxide at 25°. J. Papish observed that the vapour of tellurium introduced into a bunsen flame colours the flame blue tinged with green in its uppermost part, and a bright, metallic mirror is deposited on a cold surface held in the hottest part of the flame. The reduction of the oxides in the flame is supposed to be the cause of the characteristic luminescence. E. Blanc gave for the two **ionization constants** of tellurous acid, $K_1=2\times10^{-3}$, and $K_2=1\times10^{-8}$. R. A. Schuhmann gave for the e.m.f. of cells of the type $Te \mid TeO_2, HClO_4 \mid H_2$ −0·5286 volt at 25° and −0·5213 volt at 45°. J. J. Kasarnowsky found the conc. of tellurous ions in soln. containing increasing proportions of hydrochloric acid increases as the fourth power of the $H^{\cdot}$-ions, showing that tellurous acid acts as a weak base, $K=[Te^{\cdot\cdot\cdot\cdot}][OH']^4/[H_2TeO_3]$; or $K=1{\cdot}5\times10^{-46}$. According to A. Simek and H. Kadlocva, drops of fused tellurium dioxide on a platinum surface heated by a direct current at 800° to 950° move from the negative to the positive pole. The movement is accompanied by a deformation of the drops, the curvature of the side facing the negative pole being less than that of the other side. Under given conditions, the velocity increases as the drops become larger, but does so less rapidly than the weight of the drops. The velocity of movement and the force by which the drops are driven are both roughly proportional to the current intensity up to a certain limit. If tellurium dioxide is added to drops of fused sodium sulphate, chloride, tungstate, or pyrophosphate, the previously flattened drops become much more spherical and, under the influence of a direct current, move more rapidly than pure tellurium dioxide, a velocity of 16 cms. per sec. being sometimes attained. The direction of motion depends on the conc. of tellurium dioxide and may be reversed as the latter gradually evaporates. The phenomenon is due to changes of interfacial tension caused by potential differences. As previously indicated, the electrolysis of acidic soln. of tellurium dioxide was found by J. C. Poggendorff, L. Schucht, C. Whitehead, E. Müller, etc., to result in the deposition of black tellurium. S. Meyer gave $-0{\cdot}11\times10^{-6}$ mass unit for the **magnetic susceptibility** of tellurium dioxide, and $-0{\cdot}19\times10^{-6}$ mass unit for tellurous acid, and S. S. Bhatnagar and C. L. Dhawan, $-33{\cdot}72\times10^{-6}$ for tellurous acid, and the subject was discussed by S. S. Bhatnagar and S. L. Lather.

L. Staudenmaier found that when tellurium dioxide is heated in a current of **hydrogen,** it is slowly reduced to tellurium, and J. J. Berzelius observed that the alkali tellurites form the tellurides. F. C. Mathers and G. M. Bradbury, and V. Lenher and E. Wolesensky found that the tellurites are oxidized to tellurates when heated in **air.** D. Klein and J. Morel said that tellurium dioxide is sparingly soluble in **water,** and the aq. soln. contains one part of the dioxide in 150,000 parts of water. H. Rose said that the aq. soln. does not redden blue litmus paper; but J. J. Berzelius said that the dioxide reddens litmus after standing some time in contact with the moistened test-paper. The hydrate—tellurous acid—dissolves fairly easily in water forming a soln. which reddens litmus. If heated above 40°, the aq. soln. becomes turbid, and no longer reddens litmus owing to the deposition of fine grains of the anhydrous dioxide. When the aq. solution is evaporated at ordinary temp., it deposits the anhydrous dioxide mixed with a small proportion of the hydrate. J. J. Berzelius said that the aq. soln. of the anhydrous dioxide is tasteless, and that the aq. soln. of the hydrate has a metallic taste. P. Köthner found that **hydrogen dioxide** and **sodium dioxide** oxidize soln. of tellurites to tellurates.

J. J. Berzelius found that aq. soln. of the tellurites are oxidized by **chlorine, bromine,** and **iodine;** and, added B. Brauner, the iodine acts slowly at ordinary temp., and the reaction is complete only at 100°. R. Metzner obtained oxyfluorides by the action of **hydrofluoric acid** on tellurium dioxide; and E. B. R. Prideaux and J. O'Neil Millott, by the action of dry hydrogen fluoride on the dioxide. J. J. Berzelius found the dioxide to be sparingly soluble in most acids, but it is readily dissolved by **hydrochloric acid.** A. Ditte found that tellurium dioxide forms additive compounds with the **hydrogen halides**—*vide infra,* oxyhalides. F. A. Gooch and J. Howland observed that **hydriodic acid** reduces acidic soln. of tellurium dioxide to tellurium. F. A. Gooch and W. C. Morgan found the reaction $H_2TeO_3+4H_2SO_4+4KI=TeI_4+4KHSO_4+3H_2O$ to be quantitative; and K. Someya studied the electrometric titration of tellurous acid under these conditions. R. Schuhmann found the solubility of tellurium dioxide in $0{\cdot}7370M$-, $0{\cdot}2924M$-, and $0{\cdot}1028M$-soln. of **perchloric acid** at 25° to be respectively 5·20, 1·96, and 0·74 gram-atoms $\times 10^3$ per 1000 grms. of water.

H. B. Baker and A. H. Bennett, in their work on the at. wt. of tellurium, heated a mixture of **sulphur** and tellurium dioxide in a current of nitrogen and obtained sulphur dioxide and tellurium. W. Marckwald and A. Foizik showed that a small proportion of the sulphur is also oxidized to sulphur trioxide. According to A. Wehrle, **hydrogen sulphide** and also **ammonium sulphide** produce a black precipitate of tellurium disulphide with soln. of tellurium dioxide—the precipitate is soluble in soln. of ammonium sulphide, hydrogen sulphide, or aq. ammonia. A. Gutbier and F. Flury found that with an aq. soln. of the chloride the precipitate produced in the cold is deep orange-red, and if the soln. is hot, the precipitate is black. R. W. E. MacIvor found that with tellurites, hydrogen sulphide gives a reddish-brown precipitate which rapidly darkens in colour. An excess of **sulphur monochloride** was found by V. Lenher to react with the dioxide in accord with $TeO_2+2S_2Cl_2=TeCl_4+SO_2+3S$; and with an excess of the dioxide: $TeO_2+S_2Cl_2=TeCl_2+2S+O_2$; an excess of **thionyl chloride** forms tellurium tetrachloride, and the dichloride if the tellurium dioxide is in excess. In the cold **sulphuryl chloride** does not react with the dioxide, but when heated in a sealed tube various crystalline products are formed—*e.g.* $TeO_2:SO_2Cl_2=3:4$, $5:9$, $1:2$, and $2:5$—according to the composition of the mixture. The precipitation of tellurium from hydrochloric acid soln. by **sulphur dioxide** has been discussed in connection with selenium—Fig. 2, **10.** 58, 2. E. Divers and M. Shimose observed no reaction between **sulphur trioxide** and tellurium dioxide; B. Brauner found that warm 20 per cent. **sulphuric acid** dissolves about 0·7 per cent. of tellurium dioxide; 30 per cent. acid, about 0·85 per cent.; and 50 per cent. acid, 4·4 per cent. These soln. appear to be supersaturated because after they have stood some time, tellurium dioxide separates from the dil. acid soln., and tellurium sulphate from the conc. acid soln. E. Donath found that **sodium hyposulphite** precipitates tellurium from acid soln. of tellurium, or from soln. of tellurites. F. A. Gooch and J. Howland found that **sodium thiosulphate** is without action on cold acid soln. of tellurium dioxide, but with hot soln., tellurium is precipitated.

J. J. Berzelius said that tellurium dioxide dissolves very slowly in aq. **ammonia;** and H. Rose observed that aq. ammonia precipitates tellurous acid from soln. of tellurium salts, and the precipitate dissolves in an excess of the precipitant when the liquid is warmed. V. Lenher and E. Wolesensky obtained *pentitamminotellurous acid,* $5H_2TeO_3.NH_3$, as an intermediate stage in the decomposition of ammonium tellurite, but it is believed not to be a definite compound. According to C. Whitehead, when a soln. of a tellurite is boiled with **ammonium chloride,** tellurous acid is precipitated; while A. Gutbier and F. Flury found that when tellurium dioxide is heated with ammonium chloride, the mixture becomes yellow and then orange, and a white sublimate of $TeO_2.2HCl$ is formed. The mixture on being further heated, assumes a dark colour with the formation of a yellow sublimate. $TeCl_2.2NH_3$, which blackens on careful heating. Tellurium finally remains as a brittle mass. These phenomena do not occur when ammonium chloride is replaced by ammonium nitrate, carbonate, sulphate, phosphate, acetate, or molybdate. J. J. Berzelius found that tellurium dioxide is freely soluble in **nitric acid**; and D. Klein and J. Morel observed that boiling, dil. nitric acid dissolves some tellurium dioxide; whether or not tellurium dioxide will separate from the soln. depends on the conc. of the acid—*vide supra.* The dioxide is freely soluble in the hot, conc. acid. P. Jannasch and M. Müller, and A. Gutbier observed that acidic or alkaline soln. of tellurium dioxide are reduced to tellurium by **hydrazine salts**; whilst **phenyl hydrazine** violently reduces hydrochloric acid soln. at ordinary temp. with the evolution of heat, and the liberation of nitrogen. J. J. Berzelius found that tellurium is precipitated by **phosphorus** from acid soln. of tellurium dioxide; N. W. Fischer found that tellurium is also precipitated by alcoholic soln. of phosphorus; H. Rose, by **phosphorous acid**; and A. Gutbier, by **hypophosphorous acid.** H. Rose obtained a white precipitate by adding **sodium hydrophosphate.** V. Lenher found that **phosphorus trichloride** reduces tellurium dioxide to the element, **phosphoryl chloride** forms the complex $TeCl_4.POCl_3$; he also found that **arsenic trichloride** reacts with tellurium dioxide forming tellurium tetrachloride and arsenic trioxide. M. H. Klaproth observed that **antimony** reduces a soln. of a tellurous salt to tellurium. J. J. Berzelius, D. Klein, B. Brauner, and F. Becker found that tellurium dioxide replaces antimonyl in **potassium antimonyl tartrate** forming potassium telluryl tartrate. Tellurium dioxide reacts with **antimony trichloride** forming, according to V. Lenher, tellurium tetrachloride and antimony trioxide; **antimony pentachloride** forms the complex $TeCl_2.SbCl_5$.

J. J. Berzelius said that tellurium dioxide is decomposed by **carbon** at a comparatively low temp., and with a kind of detonation; and with alkali tellurites and carbon the alkali telluride is formed. J. J. Berzelius observed that tellurites are decomposed by the **carbon dioxide** of the atm. H. Rose observed that tellurium dioxide is reduced when fused with **potassium cyanide.** H. Rose found that acid soln. of tellurium dioxide gave no precipitate with **potassium ferro-** or **ferricyanide,** with **oxalic acid,** or with **tannin.** F. Stolba, and L. Kastner found that soln. of tellurites are completely reduced to tellurium by boiling with **glucose.** V. Lenher found that **carbon tetrachloride** has no action on tellurium dioxide. A. Oppenheim could not prepare alkyl tellurites. T. R. Glauser recommended tellurium dioxide for combustion analyses for carbon and nitrogen in dealing with aluminium nitride, calcium cyanamide, ferrosilicon, ferrochrome, hard steels, carborundum, etc. The tellurium dioxide melts to a heavy, mobile liquid in which these substances readily dissolve.

J. J. Berzelius found that copper reduces soln. of tellurium salts to the metal; M. H. Klaproth, and J. Löwe obtained a similar result with **zinc**; N. W. Fischer, with **cadmium,** and **mercury**; M. H. Klaproth, with **tin**; N. W. Fischer, with **lead**; and P. Berthier, and F. Stolba, with **iron.** N. W. Fischer added that the tellurium is usually precipitated as a black powder which by friction acquires a metallic lustre; dendritic tellurium forms when lead is used; the precipitation is usually incomplete; and a basic tellurite or basic tellurate may be formed. J. J. Berzelius found that tellurium dioxide readily dissolves in aq. soln. of **alkali hydroxides**; but in aq. soln. of the **alkali carbonates** only during a prolonged boiling; it readily dissolves when melted with alkali carbonates with the expulsion of carbon dioxide; it dissolves in fused **alkali nitrates** forming tellurates. Tellurous acid readily dissolves in aq. soln. of alkali hydroxides or carbonates, the carbon dioxide escaping only when heat is applied. According to V. Lenher and P. D. Potter, the yellowish-brown substances suspended in the fused mass before the liquid solidifies contain variable proportions of potassium tellurate and tellurium dioxide depending on the time of heating and other conditions.

According to N. W. Fischer, an ammoniacal soln. of **copper oxide** gives a greyish-blue precipitate with tellurous acid or tellurous salts. F. C. Mathers and F. V. Graham observed that **lead dioxide** converts tellurium dioxide into lead tellurate, and that the optimum temp. is 170°. H. Rose found that **barium chloride** gives a white precipitate insoluble in ammonia, but with **calcium chloride** precipitation occurs only after the addition of ammonia. A. Hilger obtained a white precipitate by adding a **magnesium salt** and ammonia to a soln. of a tellurite. N. W. Fischer found that **mercurous nitrate** gives a white precipitate; while **stannous chloride** reduces tellurous salts to tellurium which appears as a black precipitate; if the tellurous salt be very dilute, the stannous chloride produces a brown coloration which is perceptible at a dilution of 1 : 600,000. B. Brauner founded a volumetric process for the determination of tellurium on this reaction. N. W. Fischer found that **lead acetate** soln. gives a white precipitate. V. Lenher found that **lead tetrachloride** reacts with tellurium dioxide forming tellurium tetrachloride. According to B. Brauner, **chromic acid** oxidizes a hydrochloric acid or sulphuric acid soln. of tellurium dioxide to telluric acid. The reaction is slow, but is faster in hydrochloric than in sulphuric acid soln. L. Staudenmaier obtained similar results in nitric acid soln. Tellurium dioxide and the tellurites form complex salts with **molybdates, tungstates,** and **vanadates** (*q.v.*). B. Brauner observed that **potassium permanganate** oxidizes a hydrochloric or sulphuric acid soln. of tellurium dioxide, and in the latter case, with the development of oxygen: $2TeO_2+KMnO_4+4HCl=2TeO_3+MnCl_3+KCl+2H_2O$. F. A. Gooch and J. Howland studied the oxidation of tellurites to tellurates by potassium permanganate. Soln. of tervalent **manganese salts** do not oxidize tellurium dioxide. The reaction was studied by W. T. Schrenk and B. L. Browning. B. Brauner, and V. Lenher and H. F. Wakefield represented the reaction with **potassium dichromate**: $3TeO_2+K_2Cr_2O_7+8HCl=3H_2TeO_4+2KCl+2CrCl_3+H_2O$.

REFERENCES.

[1] J. J. Berzelius, *Schweigger's Journ.*, **6**. 311, 1812; **34**. 78, 1823; *Pogg. Ann.*, **28**. 392, 1833; **32**. 1, 577, 1834; W. Damiens, *Compt. Rend.*, **179**. 829, 1924; E. Divers and M. Shimose, *Journ. Chem. Soc.*, **43**. 319, 1883; J. J. Doolan and J. R. Partington, *ib.*, **125**. 1402, 1924; W. Prandtl and P. Borinsky, *Zeit. anorg. Chem.*, **62**. 237, 1909; P. Borinsky, *Ueber die Einwirkung von Schwefeltrioxyd und dessen Chlorosubstitutionsprodukten auf Schwefel, Selen und Tellur*, München, 1909.

[2] J. J. Berzelius, *Schweigger's Journ.*, **6**. 311, 1812; **34**. 78, 1823; *Pogg. Ann.*, **28**. 392, 1833; **32**. 1, 577, 1834; D. Klein and J. Morel, *Compt. Rend.*, **99**. 540, 1884; *Ann. Chim. Phys.*, (6), **5**. 59, 1885; D. Klein, *ib.*, (6), **10**. 114, 1887; P. Berthier, *ib.*, (2), **51**. 156, 1832; H. L. Wills, *Journ. Chem. Soc.*, **35**. 704, 1879; *Liebig's Ann.*, **202**. 246, 1880; O. Brunck, *ib.*, **336**. 281, 1904; F. Becker, *ib.*, **180**. 262, 1876; P. Köthner, *ib.*, **319**. 1, 1901; *Das reine Tellur und sein Atomgewicht*, Halle, 1901; H. Rose, *Pogg. Ann.*, **112**. 307, 1861; J. C. Poggendorff, *ib.*, **75**. 349, 1848; N. W. Fischer, *ib.*, **12**. 502, 1828; **13**. 257, 1828; W. Petz, *ib.*, **57**. 467, 1842; B. Brauner, *Monatsh.*, **10**. 434, 1889; **11**. 527, 1890; **12**. 34, 1891; *Sitzber. Akad. Wien*, **98**. 456, 1889; *Journ. Chem. Soc.*, **55**. 382, 1889; **59**. 58, 238, 1891; E. Divers and M. Shimose, *Journ. Chem. Soc.*, **43**. 319, 1883; E. Donath, *Zeit. angew. Chem.*, **3**. 214, 1890; A. Simek, *Chem. Listy*, **23**. 420, 1929; A. Simek and H. Kadlocva, *Rec. Trav. Chim. Pay-Bas*, **44**. 608, 1925; L. Staudenmaier, *Untersuchungen über das Tellur*, Leipzig, 1895; *Zeit. anorg. Chem.*, **10**. 197, 1895; A. Gutbier and F. Flury, *ib.*, **37**. 152, 1903; A. Gutbier and W. Wagenknecht, *ib.*, **40**. 260, 1904; A. Gutbier, *ib.*, **32**. 257, 1902; *Studien über das Tellur*, Leipzig, 1901; *Ber.*, **34**. 2724, 1901; P. Jannasch and M. Müller, *ib.*, **31**. 2377, 1898; H. Remy, *ib.*, **116**. 255, 1921; F. A. Gooch and J. Howland, *Zeit. anorg. Chem.*, **7**. 134, 1894; *Amer. Journ. Science*, (3), **58**. 375, 1894; F. A. Gooch and W. C. Morgan, *ib.*, (4), **2**. 271, 1896; F. W. Clark, *ib.*, (3), **14**. 286, 1877; G. O. Oberhelman and P. E. Browning, *ib.*, (4), **36**. 399, 1913; K. B. Heberlein, *Beiträge zur Kenntniss des Tellurs*, Basel, 1898; *Berg. Hütt. Ztg.*, **54**. 41, 1895; L. Schucht, *ib.*, **39**. 121, 1890; A. Oppenheim, *Journ. prakt. Chem.*, (1), **71**. 271, 1857, *Beobachtungen über das Tellur und einige seiner Verbindungen*, Göttingen, 1857; C. Whitehead, *Journ. Amer. Chem. Soc.*, **17**. 849, 1895; W. T. Schrenk and B. L. Browning, *ib.*, **48**. 2550, 1926; R. Schumann, *ib.*, **47**. 356, 1925; L. Pauling, *ib.*, **49**. 765, 1927; V. Lenher and P. D. Potter, *ib.*, **31**. 24, 1909; V. Lenher, *ib.*, **30**. 737, 1908; V. Lenher and E. Wolesensky, *ib.*, **35**. 718, 1913; V. Lenher and H. F. Wakefield, *ib.*, **45**. 1423, 1923; F. Stolba,

Dingler's Journ., **198**. 362, 1870 ; *Casopsis premysl Chem.*, **2**. 12, 65, 390 ; 1892 ; *Zeit. anal. Chem.*, **11**. 437, 1872 ; L. Kastner, *ib.*, **14**. 142, 1875 ; A. Hilger, *ib.*, **13**. 133, 1874 ; R. Metzner, *Ann. Chim. Phys.*, (7) **15**. 203, 1898 ; *Sur quelques composés du sélénium et du tellure*, Paris, 1898 ; J. Kasarnowsky, *Zeit. phys. Chem.*, **109**. 287, 1924 ; R. W. E. MacIvor, *Chem. News*, **87**. 209, 1903 ; M. H. Klaproth, *Mem. Akad. Berlin*, **50**. 17, 1798 ; *Beiträge zur chemischen Kenntniss der Mineralkörpen*, Berlin, **3**. 1, 1802 ; London, **2**. 1, 1804 ; *Crell's Ann.*, **1**. 91, 1798 ; *Gilbert's Ann.*, **12**. 246, 1802 ; J. Löwe, *Sitzber. Akad. Wien*, **10**. 727, 1853 ; *Journ. prakt. Chem.*, (1), **60**. 163, 1853 ; A. Wehrle, *Zeit. Phys. Math.*, (1), **9**. 133, 144, 1831 ; (2), **3**. 317, 1835 ; *Pogg. Ann.*, **21**. 599, 1831 ; *Schweigger's Journ.*, **59**. 482, 1830 ; *Isis*, 357, 1833 ; A. Schafarik, *Sitzber. Akad. Wien*, **47**. 256, 1863 ; K. Vrba, *Zeit. Kryst.*, **19**. 1, 1891 ; C. Jena, *Ueber Verbindungen, welche Vanadinsäure und tellurige Säure enthalten*, Giessen, 1907 ; S. S. Bhatnagar and S. L. Lather, *Journ. Indian Chem. Soc.*, **6**. 303, 1929 ; S. S. Bhatnagar and C. L. Dhawan, *Phil. Mag.*, (7), **5**. 536, 1928 ; S. S. Bhatnagar and R. N. Mathur, *ib.*, (7), **6**. 217, 1928 ; A. Brezina, *Ann. Nat. Hist. Mus. Wien*, **1**. 135, 1886 ; F. Beijerinck, *Neues Jahrb. Min. B.B.*, **11**. 442, 1897 ; E. Blanc, *Journ. Chim. Phys.*, **18**. 28, 1920 ; J. A. Krenner, *Termes. Kozl.*, **10**. 81, 1886 ; *Zeit. Kryst.*, **13**. 69, 1887 ; J. Nicol, *Elements of Mineralogy*, Edinburgh, 429, 1849 ; W. P. Headden, *Proc. Colorado Scient. Soc.*, **7**. 105, 1901 ; V. M. Goldschmidt, *Skrift. Nordske Akad.*, 7, 1925 ; 1, 1926 ; C. F. Rammelsberg, *Handbuch der Mineralchemie*, Leipzig, 1014, 1860 ; *Handbuch der krystallographisch-physikalischen Chemie*, **1**. 72, 1881 ; J. Esmark, *Kurze Beschreibung einer mineralogischen Reise durch Ungarn, Siebenbürgen, und das Banat*, Freiberg, 91, 1798 ; V. von Zepharovich, *Mineralogisches Lexicon für das Kaiserthum Oesterreich*, 443, 1859 ; F. A. Genth, *Proc. Amer. Phil. Soc.*, **17**. 118, 1877 ; R. Pearce, *Proc. Colorado Scient. Soc.*, **5**. 114, 1896 ; F. C. Knight, *ib.*, **5**. 66, 1896 ; W. G. Mixter, *Amer. Journ. Science*, (4), **29**. 488, 1910 ; J. Papish, *Journ. Phys. Chem.*, **22**. 430, 1918 ; S. Meyer, *Wied. Ann.*, **68**. 325, 1899 ; **69**. 236, 1899 ; *Ann. Physik*, (4), **1**. 664, 1900 ; T. R. Glauser, *Chem. Ztg.*, **38**. 187, 1914 ; *Zeit. angew. Chem.*, **34**. 154, 157, 162, 1921 ; A. Ditte, *Compt. Rend.*, **83**. 446, 1876 ; H. B. Baker and A. H. Bennett, *Journ. Chem. Soc.*, **91**. 1849, 1907 ; E. B. R. Prideaux and J. O'Neil Millott, *ib.*, **129**. 167, 520, 1926 ; W. Marckwald and A. Foizik, *Ber.*, **43**. 1710, 1910 ; A. Weller, *ib.*, **60**. B, 649, 1927 ; F. C. Mathers and F. V. Graham, *Journ. Amer. Chem. Soc.*, **51**. 3225, 1929 ; F. C. Mathers and G. M. Bradbury, *ib.*, **51**. 3229, 1929 ; K. Someya, *Science Rep. Tohoku Univ.*, **19**. 123, 1930 ; *Zeit. anorg. Chem.*, **187**. 351, 1930 ; E. Müller, *Ber.*, **36**. 4262, 1903.

§ 9. The Tellurites

Tellurous acid is dibasic forming normal *tellurites*, R_2TeO_3, and *hydrotellurites*, $HTeO_3$; as well as salts of the hypothetical *pyrotellurous acid*, $H_2Te_2O_5$; *tetratellurous acid*, $H_2Te_4O_9$; and *hexatellurous acid*, $H_2Te_6O_{13}$.

F. A. Flückiger [1] heated tellurium with aq. ammonia in a sealed tube and obtained what he regarded as **ammonium tellurite.** According to J. J. Berzelius, tellurium dioxide dissolves very slowly in aq. ammonia, while tellurous acid dissolves very quickly. On evaporating the soln. at a gentle heat, it gives off ammonia ; leaving tellurous acid contaminated with a 0·41 per cent. of ammonia. V. Lenher and E. Wolesensky said that ammonium tellurite probably exists in soln. and also in the solid state when surrounded by a sat. soln. of tellurous acid in ammonia, but on attempting to isolate it, it decomposes spontaneously at ordinary temp. forming tellurous acid, etc. They dissolved tellurium dioxide in aq. ammonia of sp. gr. 0·91, by heating the mixture in sealed tubes at 95°–100° for 10 hrs. After cooling and filtering, the soln. was allowed to evaporate spontaneously, when small crystals were obtained in the form of short needles arranged in radiating groups, or clusters of thin, transparent plates. On drying, these became opaque. They dissolved readily in ammonia, but were insoluble in water. If ammonium chloride be added to a soln. of tellurous acid in aq. ammonia, J. J. Berzelius said that what is probably **ammonium pyrotellurite,** $NH_4HTe_2O_5.12H_2O$, appears as a flocculent precipitate. The same salt is produced by adding ammonium chloride to a soln. of tellurous acid, or tellurium dichloride in warm aq. ammonia, and on adding alcohol, more of the same salt is precipitated. The pyrotellurite is decomposed by heat into ammonia, water, and tellurium dioxide.

J. J. Berzelius obtained normal **lithium tellurite,** Li_2TeO_3, by melting together equimolar proportions of tellurium dioxide and lithium carbonate, and slowly cooling the product. The aq. soln., when evaporated over conc. sulphuric acid, yields a white, earthy mass. Similarly with **lithium pyrotellurite,** $Li_2Te_2O_5$, or **lithium tetratellurite,** $Li_2Te_4O_9.nH_2O$, using the proper proportions of the components. The aq. soln. splits into the normal salt and **lithium hydropyrotellurite,** $LiHTe_2O_5.nH_2O$; the latter is also obtained from a soln. of the pyrotellurite in hot water. When heated, it intumesces as the water is driven off, and it melts as a red-heat is approached, forming a yellow liquid which, on cooling, produces a transparent glass, which behaves towards hot water like the pyrotellurite. Hot water breaks down the hydropyrotellurite forming a precipitate of tellurous acid, while a more acid tellurite passes into soln.; with cold water the crystals of tellurous acid pass into the gelatinous state, but still retain the external form of the crystals.

J. J. Berzelius prepared normal **sodium tellurite,** Na_2TeO_3, as in the case of the lithium salt, by fusing equimolar proportions of tellurium dioxide and sodium carbonate; during solidification the tellurite furnishes crystals which, according to C. F. Rammelsberg, are rhombic prisms with angles 113° to 114°. J. J. Berzelius said that the salt dissolves slowly but completely in cold water, and more quickly in hot water, from which it does not separate on cooling. Alcohol precipitates from the aq. soln. a conc. liquid which, in a few days, deposits crystals of hydrated salt. When the aq. soln. is evaporated, C. F. Rammelsberg found that rhombic prisms of the *pentahydrate,* $Na_2TeO_3.5H_2O$, are formed which lose their water at 120°. V. Lenher and E. Wolesensky also prepared this salt. They found that if to a conc. soln. of sodium tellurite about twice its vol. of 95 per cent. alcohol be added, the two liquids do not mix. There is, however, a redistribution of the water between the alcohol and the tellurite. The alcoholic layer increases in vol. by abstracting water from the tellurite soln., while the latter becomes more conc. Long standing and repeated shaking will not produce any further changes in this system. If, now, solid sodium tellurite be added, it will slowly dissolve, increasing the vol. of the tellurite soln., and withdrawing water from the alcoholic layer. But if, instead, about five vols. of absolute alcohol be added, the water is almost completely withdrawn from the sodium tellurite, and the latter is precipitated. C. Jena regarded the salt as a *hemienneahydrate,* $Na_2TeO_3.5\frac{1}{2}H_2O$. E. Blanc found that the percentage degree of hydrolysis of $0·0075N$-soln. of sodium tellurite is 0·773; and of $0·0073N$- sodium hydrotellurite, 0·0022. J. J. Berzelius prepared sodium **pyrotellurite,** $Na_2Te_2O_5$, by the fusion process as in the case of the **sodium** salt; the boiling aq. soln., when slowly cooled, furnishes pearly scales and thin six-sided plates of **sodium hydropyrotellurite,** $NaHTe_2O_5.2H_2O$, or **sodium tetratellurite,** $Na_2Te_4O_9.4H_2O$, and C. F. Rammelsberg found that the crystals lose half their water when exposed to air. V. Lenher and E. Wolesensky also prepared the pyro- and tetratellurites. They found that the pyrotellurite was oxidized by heating it for five days in air, and the tetratellurite and tellurium dioxide not at all. Hence as the proportion of tellurium dioxide in the tellurite increases, the tendency to oxidize in air decreases. According to C. F. Rammelsberg, if the normal tellurite be treated with hot water, a white crystalline powder of **sodium tritellurite,** $Na_2Te_3O_7.5H_2O$, is formed; it loses half its water at 120°, and the rest when melted. The brown, molten salt forms a transparent yellow glass when cold. By treating a soln. of the normal salt with as much nitric acid as is possible without making the liquid react acid, a precipitate of **sodium hexatellurite,** $Na_2Te_6O_{13}.8H_2O$, is formed; it is washed with cold water, and dried in air. It loses all its combined water on fusion.

J. J. Berzelius prepared normal **potassium tellurite,** K_2TeO_3, by the fusion process as in the case of the lithium and sodium salts. The white product consists of crystals with an alkaline reaction and caustic taste. V. Lenher and E. Wolesensky found that it is well to conduct the fusion in an inert atm.—say, carbon dioxide—to prevent the oxidation of tellurite to tellurate. The white, crystalline mass is deliquescent, and extremely soluble in water. The aq. soln. slowly deposits tellurous acid on exposure to air, and more readily when air is bubbled through the soln. On heating, however, the precipitate again dissolves, showing that at higher temp. tellurous acid will displace carbonic acid. When heated in air between 460°–470°, the tellurite is slowly oxidized. Thus 35·09 per cent. was converted to tellurate in 10 hrs., and 99·49 per cent. in 50 hrs. It dissolves slowly in cold water, but more rapidly in hot water; and the evaporation of the aq. soln. over sulphuric acid furnishes a syrupy mass which afterwards solidifies into a granular, non-deliquescent mass. V. Lenher and E. Wolesenky showed that potassium tellurite cannot be crystallized from aq. soln., for the aq. soln. when evaporated over sulphuric acid and solid potassium hydroxide furnishes a hard, transparent, waxy or resinous-looking homogeneous mass of the *trihydrate*, $K_2TeO_3.3H_2O$. This compound was also prepared by treating tellurium dioxide with a soln. of caustic potash, either cold or hot. The combination seems to take place only in the proportion of $2KOH : TeO_2$, so that if more than this proportion of tellurium dioxide be present, some will remain undissolved. Tellurium dioxide dissolves in hot soln. of potassium carbonate, although not so readily as in potassium hydroxide. The action of alcohol on potassium tellurite resembles its action on the sodium salt (*q.v.*). If molar proportions of the components be fused together, **potassium pyrotellurite,** $K_2Te_2O_3$, is formed as a colourless, translucent, crystalline mass; when heated in air between 460° and 470°, 26·88 per cent. was converted into tellurite in 10 hrs., and 99·47 per cent. in 57 hrs. At a rather higher temp., the tellurate loses oxygen and is reduced to tellurite, so that between 450° and red-heat, there is the reversible reaction $2K_2TeO_3+O_2\rightleftharpoons 2K_2TeO_4$. The aq. soln. is resolved by cold water into the normal tellurite which dissolves, and hydropyrotellurite which remains undissolved. Boiling water dissolves it completely, but on cooling deposits grains of the hydropyrotellurite; if the hot water also holds pyrotellurite in soln., the liquid when evaporated on the water-bath deposits the pyrotellurite as a hard, crystalline mass. If powdered tellurous acid be boiled with a soln. of potassium carbonate, the hot, filtered liquid deposits **potassium hydropyrotellurite,** $KHTe_2O_5.1\frac{1}{2}H_2O$, or **potassium tetratellurite,** $K_2Te_4O_9.4H_2O$, in regular six-sided prisms and plates; the mother-liquid yields more of the salt on evaporation and cooling; and the remaining liquid contains the normal salt in soln. The action of cold water and heat are the same as in the case of the lithium salt (*q.v.*). V. Lenher and E. Wolesensky found that the oxidation of the pyro- and tetra-tellurites in air resembles the cases with the corresponding sodium salts. According to D. Klein, if a soln. of a mol of oxalic acid, and 2 mols of potassium tellurite be mixed, and the precipitate be washed with water, and dried at 100°, **potassium hexatellurite,** $K_2Te_6O_{13}.2H_2O$, is formed as a white, amorphous powder, which melts at a dull red-heat giving off water. The heated salt may blacken owing to the reducing action of a trace of oxalic acid. It is not decomposed by water in which it is sparingly soluble.

According to J. J. Berzelius, a siskin-green precipitate of **copper tellurite** is formed by double decomposition. It is insoluble in water; turns black and gives off water when heated; readily fuses and solidifies on cooling to form a black mass with a conchoidal fraction. It is reduced on charcoal before the blow-pipe to form copper telluride. P. E. Browning and G. O. Oberhelman found that by evaporating an ammoniacal soln. of tellurous acid containing some copper salt over sulphuric acid in the presence of soda-lime, **ammonium copper tellurite,** approximating $5NH_3.CuO.9TeO_2.6H_2O$, is formed; the same salt is obtained by mixing slowly with constant stirring an ammoniacal soln. of tellurous acid and copper chloride.

J. J. Berzelius obtained **silver tellurite,** Ag_2TeO_3, by double decomposition—say from sodium tellurite and silver nitrate. It appears as a yellowish-white precipitate, soluble in ammonia. The ammoniacal soln., on evaporation, yields a basic salt. R. D. Hall and V. Lenher said that the pale yellow powder, dried at 105°, is stable in light. V. Lenher and E. Wolesensky found that the precipitate is pale yellow only when an excess of silver nitrate is used; if the sodium tellurite is in excess, the precipitate is white. When dried, both precipitates are buff-coloured, and have the same composition, but on standing, the one which was precipitated in presence of an excess of silver nitrate begins to turn dark in colour, and in the course of a week or two changes completely to a dark bluish-grey colour. The other does not change, and has actually been kept for twenty months without undergoing any modification. When silver tellurite is heated to 250° it becomes deep blue or purple in colour. This change takes place without any change in weight. On heating still higher, to 450° or 500°, it again changes to a pale yellow. In this last condition it can be cooled down to ordinary temp. unchanged, provided it is not disturbed during the cooling. But if during this cooling, and while it is still quite hot, it is disturbed by compression with a glass rod, the mass immediately changes to the purple variety. Again, when freshly precipitated silver tellurite is treated with ammonium hydroxide it dissolves immediately, and when the soln. is allowed to evaporate spontaneously brownish-yellow crystals deposit. These crystals contain neither ammonia nor water, and can be heated to 500° or higher without any change in weight. On cooling, after being thus heated, these crystals again yield the ordinary pale yellow silver tellurite. It thus appears that silver tellurite can exist in a number of different varieties. The freshly-precipitated salt is soluble in acetic and tartaric acids, also in nitric and sulphuric acids. Hydrochloric acid decomposes it with the formation of silver chloride and tellurium tetrachloride. It is insoluble in water. The precipitated tellurites have little tendency to assume the crystalline state; and no crystallization was observed by allowing precipitated silver tellurite to stand in contact with acidulated water. G. Rose obtained what is supposed to have been **silver pyrotellurite** from a soln. of silver telluride in nitric acid. The small, acuminated square prisms have an adamantine lustre; and are insoluble in water.

J. J. Berzelius obtained **calcium tellurite,** $CaTeO_3$, by heating a mixture of equimolar parts of the component oxides; the mass does not fuse at 960°; by treating alkali tellurite soln. with a calcium salt, white flecks of calcium tellurite are formed, which are sparingly soluble in cold water, and easily soluble in hot water. The evaporation of the aq. soln. gives a white earthy product of hydrolysis. **Strontium tellurite,** $SrTeO_3$, was obtained, likewise also **barium tellurite,** $BaTeO_3$. C. F. Rammelsberg also prepared the barium salt. V. Lenher and E. Wolesensky found that the white flocculent precipitate is obtained by mixing soln. of sodium tellurite and barium chloride, but it could not be obtained in the crystalline state. All the precipitates, even those obtained in dil. soln., contained chlorine which could not be washed out. The analyses ranged from $8BaTeO_3.5BaCl_2.4H_2O$ to $20BaTeO_3.\frac{1}{2}BaCl_2.20H_2O$. If a mixture of the component oxides in the theoretical proportions be heated to redness, J. J. Berzelius found that **calcium pyrotellurite,** $CaTe_2O_5$, is obtained in micaceous scales; and he found that under analogous conditions, using the theoretical proportions of the constituents, **barium tetratellurite,** $BaTe_4O_9$, could be prepared. The product appears as a transparent, colourless glass. If an aq. soln. of barium tellurite be treated with dil. nitric acid, a voluminous precipitate of the hydrate, $BaTe_4O_9.H_2O$, or **barium hydropyrotellurite,** $Ba(HTe_2O_5)_2$, is formed. It dissolves in an excess of warm nitric acid, and on evaporation of the soln., tellurium dioxide is first deposited.

According to J. J. Berzelius, white voluminous flakes of **beryllium tellurite** are produced when a soluble tellurite is added to a soln. of a beryllium salt; and **magnesium tellurite** is formed in an analogous way. V. Lenher and E. Wolesensky found that the salt is the *pentitaenneahydrate,* $5MgTeO_3.9H_2O$; and that it is only sparingly soluble, but even then it is much more soluble than the corresponding salt of the alkaline earths. The precipitate becomes granular when allowed to stand in contact with the mother-liquor. It does not vary in composition with the proportions of the salts used in its formation. When heated at different temp. to a constant weight, these results, Fig. 41, show that at about 450°, there are two phases, below that temp. the pentitaenneahydrate is stable, and above that temp., the *decitaenneahydrate,* $10MgTeO_3.9H_2O$. J. J. Berzelius obtained a white, flocculent precipitate of **zinc tellurite** by double decomposition. A. Oppenheim prepared **cadmium tellurite** as a white, gelatinous precipitate, by adding sodium tellurite to a soln. of cadmium nitrate. It dissolves in nitric acid forming a colourless soln., and in hydrochloric acid forming a yellow soln. V. Lenher and E. Wolesensky used soln. of cadmium chloride and sodium tellurite. The precipitate approximates in composition the normal tellurite, $CdTeO_3$. J. J. Berzelius obtained **mercurous tellurite** as a dark yellow precipitate which becomes brown on exposure to air, and forms **mercuric tellurite** which is also obtained by double decomposition of a soluble tellurite and a mercuric salt.

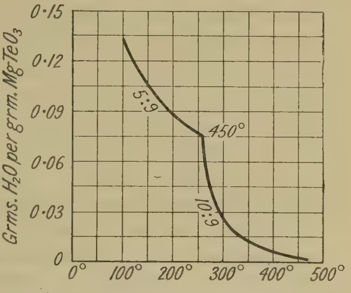


Fig. 41.—Dehydration Curve of Hydrated Magnesium Tellurite.

J. J. Berzelius reported **aluminium tellurite** to be formed as a white, flocculent precipitate on adding sodium tellurite to a soln. of an aluminium salt; it is insoluble in an excess of the aluminium salt soln. He also obtained **yttrium tellurite** in an analogous manner; and it is insoluble in an excess of the yttrium salt soln. White **zirconium tellurite** was obtained in an analogous manner; and likewise also **thorium tellurite.** J. J. Berzelius found that a basic **lead tellurite** is precipitated by the action of potassium tellurite on a soln. of lead acetate; and a white, flocculent precipitate of normal lead tellurite was also obtained; V. Lenher and E. Wolesensky mixed soln. of lead nitrate and sodium tellurite, and found that the precipitate is the tritadihydrate, $3PbTeO_3.2H_2O$. It is soluble in acids, and when heated forms the yellow, anhydrous salt; and it melts to form, on cooling, a transparent glass. It is reduced to telluride when heated with carbon. V. Lenher and E. Wolesensky found that in air at 440°–470° it oxidizes more slowly than sodium tellurite.

According to W. A. A. Prandtl, if a hydrochloric acid soln. of tellurous acid be mixed with a soln. of sodium vanadate, or if sodium tellurite and vanadate be mixed with hydrochloric acid, an orange-yellow, amorphous precipitate is produced and it rapidly dissolves if the liquor is acidic or alkaline; but if neutral a hydrated **sodium telluritovanadate** is formed. The precipitate is decomposed by water, and vanadic acid passes into soln. while tellurous acid remains undissolved. The composition of the precipitate varies with the conc. of the vanadic acid in the mother-liquor. From strongly alkaline, hot, conc. soln. of sodium tellurite and vanadate, with the former in excess, white needles of a complex salt separate out as the liquid cools. It is completely decomposed into its components when recrystallization is attempted. C. Jena treated sodium vanadate, in neutral or acidic soln., with tellurium tetrachloride, and obtained a series of complex salts. If the vanadate and tellurium tetrachloride in hydrochloric acid soln. be in the proportion $V_2O_5 : TeO_2 = 2 : 1$, and the soln. neutralized with sodium hydroxide, the complex **sodium tetravanadatopentatellurite,** $Na_2O.2V_2O_5.5TeO_2.2H_2O$, is formed; if in the proportion 1 : 1, the complex **sodium tetravanadatohexatellurite,** $Na_2O.2V_2O_5.6TeO_2.12H_2O$, when dried at 100° the *dihydrate* is formed, and when dried over sulphuric acid in vacuo, the *trihydrate;* and if the proportion be 1 : 5, **sodium tetravanadatodecatellurite,** $Na_2O.2V_2O_5.10TeO_2.3H_2O$, is formed. By working in alkaline soln., with 20 grms. of tellurium dioxide and 2 grms. of vanadium pentoxide and the mixture neutralized with sodium hydroxide, **sodium hexavanadatotellurite,** $Na_2TeO_3.6Na_3VO_4.20H_2O$, is formed; with 40 grms. of tellurium dioxide and 5 grms. of vanadium pentoxide, **sodium divanadatopentatellurite,** $5Na_2TeO_3.2Na_3VO_4.52H_2O$, is formed; the conc. of the mother-liquor yields what is supposed to be a mixture of **sodium divanadatotetratellurite,** $4Na_2TeO_3.2Na_3VO_4.48H_2O$, and of **sodium divanadatotritellurite,** $3Na_2TeO_3.2Na_3VO_4.44H_2O$.

J. J. Berzelius prepared **chromium tellurite,** as a pale greyish-green precipitate, by adding a soluble tellurite to a soln. of a chromic salt; it is soluble in an excess of the latter. O. W. Gibbs made some preliminary observations on the **tellurito-**

molybdates analogous to the selenomolybdates; and on the **telluritotungstates** analogous to the selenitotungstates. According to D. Klein, tellurous acid dissolves readily in soln. of sodium, ammonium, or potassium paratungstate, yielding in the first case micaceous crystals and a dense mother-liquor. This mother-liquor gives no precipitate with hydrochloric acid in the cold, and is only decomposed after several successive evaporations to dryness with this acid. The mother-liquor contains tellurous acid, which is precipitated only by sulphurous acid or sodium hydrosulphite in the cold, after the addition of hydrochloric acid. The action of tellurous acid on ammonium or potassium paratungstate yields no crystalline products, but only a pulverulent deposit, which contains tungstic and tellurous acids, and behaves like a tungstotellurite. J. J. Berzelius obtained by double decomposition pale lemon-yellow, insoluble **uranyl tellurite.**

J. J. Berzelius, and V. Lenher and E. Wolesensky obtained a white or faintly pink, flocculent precipitate of **manganese tellurite,** by mixing sodium tellurite with a soln. of manganese chloride. The salt is very unstable. On standing, the colour gradually changes to a deep chocolate-brown. The change takes place more rapidly when the mixture is brought into direct contact with air. This change is due to oxidation of the manganese to the tervalent state. When the chocolate-coloured substance is treated with hydrochloric acid, a dark, greenish-brown soln. of manganic chloride is formed. This colour is discharged by diluting the soln. with water, or by boiling; in the latter case chlorine is evolved. If the precipitation is carried out with soln. which have been previously thoroughly boiled to expel the air, the precipitate is perfectly white, and remains so as long as contact with air is avoided. The freshly-precipitated manganese tellurite is more sensitive to oxidation than when it has stood some time. J. J. Berzelius obtained by double decomposition **ferrous tellurite** in yellowish-grey flakes; and **ferric tellurite** in yellow flakes. E. S. Dana and H. L. Wells found greenish-yellow masses or small mamillary forms of a mineral in the El Plombo mine, Tegucigalpa, Honduras; and it was named **durdenite**—after H. S. Durden. The analysis corresponds with the *tetrahydrate*, $Fe_2(TeO_3)_3.4H_2O$. The hardness is 2·0 to 2·5. W. F. Hillebrand also described a yellowish-green hydrated ferric tellurite from Tombstone, Arizona, which occurs in thin scales, probably monoclinic. The (010)-cleavage is perfect. The mineral was called **emmonsite**—after S. F. Emmons. Its exact composition is unknown. The ratios $Fe_2O_3 : TeO_2 : H_2O$ are 3·16 : 1 : 1·77. The hardness is about 5. **Cobalt tellurite** is a dark purple precipitate; V. Lenher and E. Wolesensky found that the precipitate is *monohydrated*, $CoTeO_3.H_2O$, and melts between 300° and 400° without changing colour, but with the loss of its water of crystallization. J. J. Berzelius obtained by double decomposition **nickel tellurite** in pale greenish-white flakes. V. Lenher and E. Wolesensky found that the precipitate is *monohydrated*, $NiTeO_3.H_2O$, and when heated, loses water and turns light brown.

REFERENCES.

[1] J. J. Berzelius, *Schweigger's Journ.*, **6.** 311, 1812; **34.** 78, 1823; *Pogg. Ann.*, **28.** 392, 1833; **32.** 1, 577, 1834; F. A. Flückiger, *Pharm. Viertelj*, **12.** 332, 1863; C. F. Rammelsberg, *Sitzber. Akad. Berlin*, 382, 1875; D. Klein, *Ann. Chim. Phys.*, (6), **10.** 112, 1887; *Bull. Soc. Chim.*, (2), **42.** 169, 1884; V. Lenher and E. Wolesensky, *Journ. Amer. Chem. Soc.*, **35.** 718, 1913; R. D. Hall and V. Lenher, *ib.*, **24.** 918, 1902; P. E. Browning and G. O. Oberhelman, *Amer. Journ. Science*, (4), **36.** 399, 1913; G. Rose, *Pogg. Ann.*, **18.** 60, 1830; A. Oppenheim, *Beobachtungen über das Tellur und einige seiner Verbindungen*, Göttingen, 1859; *Journ. prakt. Chem.*, (1), **71.** 278, 1857; O. W. Gibbs, *Amer. Chem. Journ.*, **17.** 167, 1895; *Ber.*, **18.** 1089, 1895; W. A. A. Prandtl, *Verbindungen höherer Ordnung zwischen den Oxyden RO_2 und R_2O_5*, München, 46, 1906; E. S. Danz and H. L. Wells, *Amer. Journ. Science*, (3), **40.** 80, 1890; W. F. Hillebrand, *Proc. Colorado Scient. Soc.*, **2.** 20, 1885; E. Blanc, *Journ. Chim. Phys.*, **18.** 28, 1920; C. Jena, *Ueber Verbindungen, welche Vanadinsäure und Tellurigesäure enthalten*, Giessen, 1907; G. Jander, *Ueber die Tellursäure und ihre Alkalisalze in ihrem Verhalten als Halbkolloide*, Berlin, 1917; A. Rosenheim and G. Jander, *Koll. Zeit.*, **22.** 23, 1917.

§ 10. Tellurium Trioxide and the Telluric Acids

J. J. Berzelius[1] said that when telluric acid is heated above 360°, but not to a red-heat, **tellurium trioxide,** TeO_3, remains. If the temp. be too high, the trioxide decomposes into the dioxide, when the product instead of being orange-yellow is white. If tellurium dioxide has been formed, it can be dissolved out by means of hydrochloric acid. L. Staudenmaier said that the last traces of water are given off very slowly. Tellurium trioxide obtained in this way is orange-yellow, and the granules retain the form of the crystals of orthotelluric acid from which it was derived. F. W. Clarke said that the sp. gr. is 5·07 at 14·5° ; 5·08 at 10·5° ; and 5·11 at 11°. It decomposes when heated to dull redness, the m.p. of tellurium dioxide, giving off oxygen and forming the dioxide. The trioxide is insoluble in cold and hot water ; cold hydrochloric acid, hot nitric acid, and moderately conc. potash-lye are without action ; hot, conc. hydrochloric acid decomposes it with the evolution of chlorine ; and very conc., hot potash-lye dissolves it with the formation of tellurates.

The tellurium in the trioxide is probably sexivalent like sulphur in sulphur trioxide. The hydrate, $TeO_2.3H_2O$, sometimes regarded as *dihydrated telluric acid,* $H_2TeO_4.2H_2O$, behaves as if it were **orthotelluric acid,** H_6TeO_6 ; while the hydrate, $TeO_2.H_2O$, generally called telluric acid, H_2TeO_4, is **metatelluric acid.** This acid appears as the *dihydrate—i.e.* orthotelluric acid—and the *hexahydrate,* $H_2TeO_4.6H_2O$. F. C. Mathers and F. V. Graham obtained telluric acid by the action of sulphuric acid on lead tellurate ; and F. C. Mathers and G. M. Bradbury, by the action of conc. nitric acid on calcium tellurate. This latter may be the *tetrahydrate of orthotelluric acid,* $H_2TeO_2.4H_2O$. F. Mylius obtained the following results for the percentage solubility, *S* :

	0°	5°	10°	15°	10°	30°	60°	100°	100°
S .	13·92	17·84	26·21	32·79	25·29	33·36	43·67	60·84	c. 67
Solid phase	$H_2TeO_4.6H_2O$				$H_2TeO_4.2H_2O$				

The solubility expressed in mols. of H_2TeO_4 per 100 mols. of water is illustrated by Fig. 39. There is a transition temp. at 10° ; and the eutectic temp. is at —1·5°, although the hexahydrate is readily undercooled to —8°. L. Staudenmaier, and F. Mylius found that the crystals of the hexahydrate resemble those of potassium dihydrophosphate, and belong to the tetragonal system. They effloresce when dried between filter-paper, and pass into the orthotelluric acid by the heat of the hand. H. Remy discussed the structure of orthotelluric acid, H_6TeO_6.

The equilibrium conditions of orthotelluric acid, H_6TeO_6, or $H_2TeO_4.2H_2O$, are indicated in Fig. 42 ; and the acid is obtained by the spontaneous crystallization of aq. soln. The aq. soln. was prepared by J. J. Berzelius, H. L. Wells, and B. Brauner by dissolving tellurium in aqua regia. A. Mailfert obtained the acid by oxidizing tellurium with ozone in the presence of moisture ; A. Gutbier and F. Resenscheck, by oxidizing tellurium in alkaline soln. by hydrogen dioxide. A. Gutbier and W. Wagenknecht said that potassium tellurate is produced when a 15 per cent. soln. of hydrogen dioxide acts on a mixture of potassium hydroxide and tellurium dioxide at 60°–70°. When the soln. is acidified by sulphuric acid, telluric acid is precipitated and may be obtained free from potassium salts. Sodium hydroxide soln. may be substituted for potassium hydroxide. F. Becker oxidized tellurium dioxide with lead dioxide in nitric acid soln. The lead is afterwards removed by sulphuric acid, but, added L. Staudenmaier, it is difficult to free the telluric

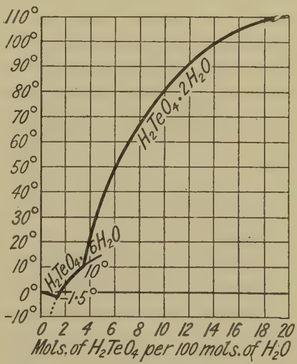


FIG. 42.—The Solubility of Telluric Acid in Water.

acid from lead and sulphuric acid. J. J. Berzelius oxidized tellurium dioxide to the trioxide by fusion with alkali nitrates; A. Oppenheim, by fusion with potassium chlorate; J. J. Berzelius, and P. E. Browning and H. D. Minnig, by the action of chlorine; L. Staudenmaier, by the action of bromine on silver tellurite: $Ag_2TeO_3+Br_2+H_2O=H_2TeO_4+2AgBr$; B. Brauner, by the action of iodine in alkaline soln.; B. Brauner, by the action of chromic acid in hydrochloric or sulphuric acid soln.; L. Staudenmaier, by the action of chromic acid in nitric acid soln.

The soln. of the element in aqua regia is freed from nitric acid by evaporation with an excess of hydrochloric acid. The soln. is diluted, filtered, and the tellurium precipitated by sodium bisulphite, and well washed with hot water. The moist tellurium is oxidized with nitric acid, and the resulting basic nitrate purified by recrystallization The basic nitrate is covered with several times its bulk of dil. nitric acid, and chromic anhydride slightly in excess of that required by the equation: $3TeO_2+2CrO_3+3H_2O=3H_2TeO_4+Cr_2O_3$ is added. The liquid is boiled and then evaporated until a crust forms on the surface. The crystals are removed from the cold soln. and the latter again evaporated. The operation is continued as long as telluric acid separates from the mother liquid. The acid is dissolved in hot water—if a white residue remains undissolved chromic anhydride insufficient to oxidize the tellurium dioxide is used. The acid must now be recrystallized a number of times in order to remove the chromium nitrate. The yield is about 80 per cent.

A. Gutbier and F. Flury found that when telluric acid is prepared by oxidizing a nitric acid soln. of tellurium dioxide with chromic acid, dark purple crystals of hydrated chromic nitrate, $Cr(NO_3)_3.9H_2O$, separate if too much chromic acid is used and they contain a very small quantity of telluric acid or tellurium nitrate. To obtain pure telluric acid, it is necessary to avoid excess of chromic acid; the telluric acid so obtained is quite colourless. Telluric acid should not be separated from a soln. containing sulphuric acid, for the solid substance retains this acid with great tenacity. J. Meyer and H. Moldenhauer obtained orthotelluric acid as a crystalline, snow-white powder, readily soluble in water, by oxidizing tellurium tetrachloride with chloric acid in the following manner:

Tellurium (10 grms.) is boiled with 10 c.c. of nitric acid and 3 c.c. of hydrochloric acid until completely dissolved. To the hot soln. is added gradually a conc. soln. of 9 grms. of chloric acid and the soln. is boiled until no more chlorine is evolved. A slight excess of chloric acid is added to avoid formation of any explosive chlorine oxide. The soln. is filtered through asbestos and concentrated by distillation in a vacuum on the water-bath, thereby removing chlorine. The telluric acid can be crystallized out by the addition of conc. nitric acid, collected, and finally freed from chlorine and nitrogen oxides by drying in vacuo.

J. Meyer and W. Franke modified this process. B. Brauner obtained telluric acid by the action of potassium permanganate in acidic or alkaline soln.; and K. B. Heberlein, by the anodic oxidation of a soln. of tellurium dioxide in nitric acid. P. E. Browning and H. D. Minnig tested if all the tellurous acid has been oxidized to telluric acid by making the soln. alkaline, and acidifying with acetic acid. If the soln. remains clear the oxidation to telluric acid is complete. S. Ghosh and N. R. Dhar, and W. von Behren and J. Traube studied the colloidal soln. of telluric acid.

The colourless **crystals** of orthotelluric acid were analyzed by L. Staudenmaier, and A. Gutbier. They occur in two forms—cubic and monoclinic. If a hot aq. soln. of orthotelluric acid be mixed with nitric acid a mixture of both forms of crystals is obtained. J. J. Berzelius described the crystals formed by the spontaneous evaporation of the aq. soln. as colourless, flattened, six-sided prisms with very obtuse summits, and often striated longitudinally; and if they separate from a soln. containing sulphuric acid, or from a warm, conc. soln., they are said to be short eight-sided prisms. W. Muthmann, and O. Brunck, and A. Gutbier thought these crystals were trigonal. The crystals were also studied by A. Oppenheim, L. Finckh, and A. Handl. B. Gossner obtained the monoclinic crystals by the slow evaporation of the aq. soln., or by cooling a warm, dil. nitric acid soln., and found the axial ratios to be $a:b:c=0·6104:1:0·5206$, and $\beta=104° 30'$. **Twinning,** and trilling occur about the (110)-plane; and fourlings were also observed. The

(010)-**cleavage** is clear. The **optical character** is positive; and the **optic axial angle** $2V=47° 30'$. The cubic crystals were observed by J. W. Retgers, and L. Staudenmaier. B. Gossner obtained the cubic forms in small singly refracting octahedra from a soln. of telluric acid in hot nitric acid of sp. gr. 1·32. They are accompanied by some monoclinic crystals—but the proportion of these decreases with the increasing conc. until finally only the cubic form appears. L. M. Kirkpatrick and L. Pauling found that the **X-radiogram** of the octahedral crystals corresponds with a face-centred, cubic lattice, with edge 15·48 A. A transformation of monoclinic to cubic crystals was not observed at temp. up to 130°; but the reverse transformation has been reported. P. Niggli discussed the **electronic structure** of the tellurates.

F. W. Clark gave for the **specific gravity** of ordinary orthotelluric acid, 3·00 at 25·5°; 2·965 at 26·5°. B. Gossner gave for the monoclinic crystals 3·071, and for the cubic crystals 3·053. Observations on the f.p. and b.p. of aq. soln. of telluric acid agree with measurements of the electrical conductivity. Irregularities in the b.p. measurements indicate the formation of some colloidal telluric acid. The abnormally large values for the temp. coeff. of the conductivity show that the complexity of the solute changes with rise of temp., so that the more complex modification which forms at the higher temp. is more strongly ionized. *Allo*telluric acid represents such a modification with a high conductivity. The fall in the conductivity of soln. of telluric acid at 25° continues until the value is characteristic of the crystallized acid. The depolymerization is also shown by the turbidity indicating the formation of a colloidal, insoluble modification. *Allo*telluric acid is therefore supposed to be not homogeneous, but rather a mixture of polymerized forms differing in complexity. J. O. Perrine observed no ultra-violet fluorescence when telluric acid crystals are exposed to X-rays for 5 hrs. S. Ghosh and N. R. Dhar studied the **viscosity** of colloidal soln. of telluric acid.

According to J. J. Berzelius, the **action of heat** on orthotelluric acid is such that it loses no water at 100°; and, according to L. Staudenmaier, none at 90°; but P. Köthner said that the acid loses some water when it is dried on the water-bath at 100°. J. J. Berzelius said that 2 mols. of water are lost at 160°, and L. Staudenmaier, 2 mols. at 140°. A. Gutbier found that when the acid is heated for half an hour at 110°–115°, it loses 8·00 per cent. of water—one mol is eq. to 7·84 per cent.; and in 2 hrs. at this temp. 9·14 per cent. of water is lost; when heated at 145°, until its weight is constant, the acid loses 13·20 per cent.; 17·01 per cent. at 170°; and when heated over the bunsen flame, 30·50 per cent. is lost. This corresponds with the transformation of orthotelluric acid to tellurium dioxide. A. Gutbier found that the **lowering of the freezing point** of water by the soln. of 0·3242 grm. of telluric acid in 20·1388 grms. of solvent is 0·140°, so that the mol. wt. of the acid is 218·5. The theoretical value for H_6TeO_6 is 229, and for H_2TeO_4, 193·6. From (i) the lowering of the f.p. of aq. soln.; (ii) the behaviour of the acid when heated; (iii) the ready passage of the hydrate $H_2TeO_4.6H_2O$ or $H_6TeO_6.3H_2O$ into H_6TeO_6; and (iv) the fact that unlike acids of the type H_6TeO_4, telluric acid it is not esterifiable, A. Gutbier inferred that both mols. of water in the hydrate $H_2TeO_4.2H_2O$ are constitutional so that the formula is H_6TeO_6, or $Te(OH)_6$. The powdered acid was found by L. Staudenmaier, and P. Köthner to lose no water over phosphorus pentoxide in vacuo. W. G. Mixter gave for the **heat of formation** $(Te,3O)=83·6$ Cals. According to R. Metzner, the **heat of solution** of the ortho-acid is −3·35 Cals.; but the heats of soln. of the meta-acid, and of the anhydride could not be determined. A. Gutbier found the **heat of neutralization** per mol is 13·38 Cals. F. Urban and V. W. Meloche used the refractometer for measuring the concentration of soln. of telluric acid. H. Nisi studied the Raman effect with the tellurates.

A. Rosenheim and G. Jander found the mol. **electrical conductivity,** μ, of aq. soln. containing a mol of H_2TeO_4 in v litres of water at 25° to be:

v .	4	8	16	32	64	128	256	513	1024
μ .	0·1902	0·1984	0·2029	0·2119	0·2245	0·2611	0·3131	0·4460	0·6913

Measurements of the H-ion concentration of the normal acid gave $[H^{\cdot}]=4\times10^{-5}$ gram-ion per litre at 25°. Assuming that the acid ionizes in accord with $H_6TeO_6 = H^{\cdot}+H_5TeO_6'$, this gives $K=1{\cdot}6\times10^{-4}$ for the ionization constant. Hence, orthotelluric acid is a very weak acid approximating boric and hydrocyanic acids. This is in agreement with the low values for the mol. conductivity. A. Miolati and E. Mascetti also followed the conductivity of the acid while being treated with progressive additions of sodium hydroxide. Measurements were also made by A. Gutbier. E. Blanc obtained for the **ionization constants** $K_1=6\times10^{-7}$, and $K_2=4\times10^{-11}$. As J. J. Berzelius showed, telluric acid is a feeble acid for it reddens blue litmus very feebly ; and A. Gutbier said that its **acidity** is about the same order as that of hydrogen sulphide or cyanide. K. B. Heberlein, and A. Gutbier said that telluric acid is so weak an acid that it cannot be titrated in the ordinary way, but with phenolphthalein in the presence of glycerol, K. B. Heberlein said that it can be titrated with sodium or potassium hydroxide soln. D. D. Karve said that ordinary telluric acid is inactive towards ethyl diazoacetate, and the indicator dimethylaminoazobenzene, and hence possesses the formula of a true acid, $Te(OH)_6$; *allo*-telluric acid is also a true acid ; but the so-called metatelluric acid behaves like a pseudo-acid so that its constitution is $O{=}Te(OH)_2{=}O$. F. Jirsa studied the effect of telluric acid on the potential of the silver anode. A. Oppenheim said that the ortho-acid is **diamagnetic.**

Ortho-telluric acid, said J. J. Berzelius, has a metallic not an acid taste. A. Oppenheim found that the tellurates are reduced to tellurides when heated with hydrogen. Orthotelluric acid is soluble in hot and cold **water ;** and F. Mylius' observations on the solubility are indicated above, Fig. 42. If the aq. soln. be evaporated on a water-bath to a syrupy consistency, the soln. crystallizes on cooling ; but if it be evaporated to dryness, an opaque, non-crystalline or glassy mass is produced which J. J. Berzelius found to dissolve in water very slowly. A. Gutbier made a similar observation ; and F. Mylius found that the slow-dissolving telluric acid is produced when orthotelluric acid is treated with conc. sulphuric acid at 60° to 90°. F. Mylius observed that the soln. have a great tendency to supersaturation during cooling. A. Gutbier and F. Flury observed that when aq. soln. of telluric acid are evaporated, a turbidity may be produced, but the suspension is so fine that it easily passes through a filter. The telluric acid may, however, separate as a gelatinous, voluminous mass. This substance has been dried in a desiccator and by heating at various temp., but no proof could be found of the existence of the telluric acid H_2TeO_4. The results obtained indicate that, besides telluric acid, H_6TeO_6, and its known, easily-soluble hydrate, there exist other difficultly-soluble hydrates, which all, however, lose water easily when heated, and give tellurium dioxide as the final residue. P. Köthner said that telluric acid volatilizes with steam when boiled with water ; but A. Gutbier denied this. The sat. aq. soln. was found by L. Staudenmaier to give a precipitate of the ortho-acid when treated with nitric acid ; and J. J. Berzelius obtained a similar result by the addition of alcohol. J. J. Berzelius found that telluric acid dissolved in cold, conc. **hydrochloric acid** can be evaporated at ordinary temp. without changing the telluric acid, but at 40°–45°, chlorine is evolved and the telluric acid is reduced to tellurium dioxide. F. A. Gooch and J. Howland found that telluric acid, in dil. sulphuric acid soln., is reduced to tellurium dioxide and tellurium by **hydriodic acid,** and to tellurium by **hydrobromic acid** in boiling soln. E. B. Benger found that with **sulphur,** in a sealed tube at 110°, a 30 per cent. aq. soln. of telluric acid is incompletely reduced ; with **selenium,** under similar conditions, tellurous and selenious acids are formed ; and with **tellurium,** tellurous acid is produced. The reducing action of **hydrogen sulphide** has been previously discussed ; the reaction was studied by A. Oppenheim, F. Becker, B. Brauner, L. Staudenmaier, A. Gutbier and co-workers, and E. B. Benger—*vide infra,* tellurium sulphides. B. Brauner found that **sulphur dioxide** in a sealed tube with an aq. soln. of telluric acid reduces it only partially to tellurium. E. B. Benger obtained confirmatory results. O. Brunck found that telluric acid or tellurates are reduced to tellurium by **sodium hyposulphite.** A. Gutbier and F. Flury found that a mixture of telluric acid or its salts with **ammonium chloride** behaves, when heated, like the mixture with ammonium chloride and tellurium dioxide (*q.v.*). P. Jannasch and M. Müller found that **hydrazine sulphate** precipitates tellurium in hydrochloric acid soln., but not so with nitric acid soln. The precipitation is quantitative when ammoniacal soln. are treated with hydrazine or **hydroxylamine.** A. Gutbier found that hydrazine hydrate, or **phenylhydrazine** assisted by heat reduces telluric acid quantitatively to tellurium; likewise also **hypophosphorous acid.** R. F. Weinland and H. Prause also found that the tellurates form complex salts with **phosphates** and **arsenates**—*vide infra.* J. J. Berzelius said that tellurates are reduced with feeble detonation when heated with **carbon,** and tellurides are formed. J. J. Berzelius found that when a tellurate is heated to redness with **potassium,** potassium telluride is formed, but not so with silver and zinc tellurates. Although telluric acid is so feeble an acid, E. B. Hutchins found that a hot conc. soln. will attack **arsenic, antimony** and **bismuth,** as well as many other metals—*e.g.* **silver, zinc, cadmium, mercury, aluminium, tin, lead,** and **nickel.** F. W. Clarke said that **thallium** is not attacked by a boiling soln. of telluric acid. F. Hundeshagen found that soluble gold chloride is produced by the action of **gold** on a hydrochloric acid soln. of telluric acid.

According to J. J. Berzelius, **metatelluric acid,** H_2TeO_4, is formed by heating the higher hydrate to 160° when the crystals are converted without change of form into an opaque mass which is yellow when hot, and white when cold. L. Staudenmaier found that the dehydration begins at 140°, and is at first rapid, then so slow that a week is not sufficient for the dehydration. At a higher temp., some telluric acid is decomposed. A. Gutbier could not prepare metatelluric acid; he assumed that it does not exist; the colourless telluric acid of J. J. Berzelius, and the yellow telluric acid of B. Brauner are said to be mixtures of tellurium trioxide and orthotelluric acid. K. B. Heberlein stated that if ordinary crystalline telluric acid be heated in a current of water vapour to 200°–210°, the product is 99 per cent. H_2TeO_4. According to F. W. Clarke, the sp. gr. of the white, flocculent metatelluric acid is 3·42 at 18·8°, 3·46 at 19·1°, and 3·44 at 19·2°. J. J. Berzelius, and L. Staudenmaier said that if the meta-acid be heated below redness, it gives off water forming tellurium trioxide; and at a red-heat, it is resolved into water, oxygen, and tellurium dioxide. L. Staudenmaier said that when heated in a current of hydrogen, it is reduced to tellurium, slowly at 300°, rapidly at a red-heat. J. J. Berzelius found that the meta-acid is very slowly but completely soluble in cold water, and is quickly dissolved by hot water.

TABLE I.—REACTIONS OF ALLOTELLURIC AND ORTHOTELLURIC ACIDS.

Reagents, etc.	Orthotelluric acid.	Allotelluric acid.
Taste	Sweet, metallic	Acidic
Alcohol	White pp. H_6TeO_6	No pp.
Congo red	Red	Blue
N-NaOH	No pp.	White pp. soluble in excess
Sod. carb.	No pp.	White pp. not soluble in excess.
Sod. silicate . . .	No pp.	White pp.
N-KOH	Soluble pp.	Sparingly soluble pp.
Pot. carb.	Soluble pp.	Sparingly soluble pp.
Aq. ammonia . . .	Soluble pp.	Sparingly soluble pp.
Guanidine carbonate . .	No pp.	White pp.
Albumin	No pp.	White pp.
Sodium thiosulphate . .	No pp. at first.	Separation of sulphur; brown pp.

F. Mylius found that when orthotelluric acid, H_6TeO_6, is heated to 140° it is converted into what he called **allotelluric acid**; and this is thought to be **trimeta-**

telluric acid, $(H_2TeO_4)_3$. It fuses at ordinary temp. giving a sticky, colourless mass which is miscible with water in all proportions. In the course of some months' contact with water, it furnishes crystals of orthotelluric acid. A comparison of the behaviour of allotelluric and orthotelluric acids towards some reagents is indicated in Table I. The albumin reaction with allotelluric acid is sensitive to one part of the acid in 5,000 parts of water. Cryoscopic determinations of aq. soln. show that the mol. wt. corresponds with $(H_2TeO_4)_{2\cdot 9}$. The action of water is slowly to resolve the complex into simpler mols. as in the analogous case of the polymetaphosphoric acids. The conductivity of allotelluric acid is five times as great as that of orthotelluric acid and allotelluric acid is, therefore, much the stronger acid. The electrical conductivity of a soln. of 0·089 grm. $(H_2TeO_4)_n$ per c.c. of water, initially K=0·0040, falls rapidly to 0·000071 in the course of a few days. D. Karve said that the absorption spectra agree with the assumption that ordinary telluric acid is $Te(OH)_6$; that metatelluric is a pseudo-acid of the constitution $(HO)_2TeO_2$; and allotelluric acid is a true acid, H_2TeO_4.

According to R. Metzner, if a soln. of tellurium dioxide in orthotelluric acid be slowly evaporated large prisms of orthotelluric acid, and small opaque, white spheres composed of small acicular crystals, of the composition *tellurosic oxide*, $2TeO_2.TeO_3$, or *tellurium tritaheptoxide*, Te_3O_7, or *telluryl tellurite*, $TeO(TeO_3)_2$, are formed. V. Lenher and E. Wolesensky also observed that in the oxidation of potassium pyrotellurite, the potassium tellurosate, $K_2O.TeO_3.TeO_2$, is formed as an intermediate compound.

REFERENCES.

[1] J. J. Berzelius, *Schweigger's Journ.*, **6**. 311, 1812 ; **34**. 78, 1823 ; *Pogg. Ann.*, **28**. 392, 1833 ; **32**. 1, 577, 1834 ; L. Staudenmaier, *Untersuchungen über das Tellur*, Leipzig, 1895 ; *Zeit. anorg. Chem.*, **10**. 197, 1895 ; D. D. Karve, *Journ. Indian Chem. Soc.*, **2**. 128, 1925 ; F. W. Clarke, *Amer. Journ. Science*, (3), **14**. 286, 1877 ; (3), **16**. 206, 401, 1878 ; F. Mylius, *Ber.*, **34**. 2208, 1901 ; K. B. Heberlein, *Beiträge zur Kenntniss des Tellurs*, Basel, 1898 ; *Berg. Hütt. Ztg.*, **54**. 41, 1895 ; B. Brauner, *Journ. Chem. Soc.*, **67**. 550, 1895 ; W. G. Mixter, *ib.*, (6), **29**. 488, 1910 ; F. A. Gooch and J. Howland, *ib.*, (3), **48**. 375, 1894 ; *Zeit. anorg. Chem.*, **7**. 132, 1894 ; H. Remy, *ib.*, **116**. 255, 1921 ; A. Gutbier, *Studien über das Tellur*, Leipzig, 17, 1901 ; *Ber.*, **34**. 2724, 1901 ; *Ber. phys. med. Soc. Erlangen*, **37**. 278, 1905 ; *Zeit. anorg. Chem.*, **32**. 257, 1902 ; A. Gutbier and W. Wagenknecht, **40**. 260, 1904 ; A. Gutbier and F. Resenscheck, *ib.*, **42**. 174, 1906 ; A. Gutbier and F. Flury, *ib.*, **37**. 152, 1903 ; W. Muthmann, *ib.*, **10**. 191, 1895 ; R. F. Weinland and H. Prause, *ib.*, **28**. 45, 1901 ; *Ber.*, **33**. 1015, 1900 ; H. Prause, *Ueber Verbindungen der Tellursäure mit Jodaten, Phosphaten und Arsenaten*, Leipzig, 1901 ; J. Meyer and H. Moldenhauer, *Zeit. anorg. Chem.*, **119**. 132, 1921 ; J. Meyer and W. Franke, *ib.*, **193**. 191, 1930 ; A. Oppenheim, *Journ. prakt. Chem.*, (1), **71**. 271, 1857 ; *Beobachtungen über das Tellur und einige seiner Verbindungen*, Göttingen, 1857 ; P. Köthner, *Liebig's Ann.*, **319**. 1, 1901 ; *Das reine Tellur und sein Atomgewicht*, Halle, 1901 ; H. L. Wells, *Journ. Chem. Soc.*, **35**. 704, 1879 ; *Liebig's Ann.*, **202**. 246, 1880 ; F. Becker, *ib.*, **180**. 258, 1876 ; F. Hundeshagen, *Chem. Ztg.*, **29**. 799, 1905 ; R. Metzner, *Ann. Chim. Phys.*, (7), **15**. 203, 1898 ; *Sur quelques composés du sélénium et du tellure*, Paris, 1898 ; A. Mailfert, *Compt. Rend.*, **94**, 1186, 1882 ; B. Gossner, *Zeit. Kryst.*, **38**. 498, 1904 ; L. M. Kirkpatrick and L. Pauling, *ib.*, **63**. 502, 1926 ; O. Brunck, *Liebig's Ann.*, **536**. 281, 1905 ; *Ber.*, **34**. 2735, 1901 ; P. Jannasch and M. Müller, *ib.*, **31**. 2377, 1898 ; J. W. Retgers, *Zeit. phys. Chem.*, **8**. 70, 1891 ; A. Handl, *Sitzber. Akad. Wien*, **32**. 242, 1859 ; E. Blanc, *Journ. Chim. Phys.*, **18**. 28, 1920 ; A. Miolati and E. Mascetti, *Gazz. Chim. Ital.*, **31**. i, 93, 1901 ; E. B. Hutchins, *Journ. Amer. Chem. Soc.*, **27**. 1157, 1905 ; E. B. Benger, *ib.*, **39**. 2179, 1917 ; V. Lenher and E. Wolesensky, *ib.*, **35**. 718, 1913 ; F. Urban and V. W. Meloche, *ib.*, **50**. 3003, 1928 ; F. C. Mathers and F. V. Graham, *ib.*, **51**. 3225, 1929 ; F. C. Mathers and G. M. Bradbury, *ib.*, **51**. 3229, 1929 ; G. Jander, *Ueber die Tellursäure und ihre Alkalisalze in ihren Verhalten als Halbkolloide*, Berlin, 1917 ; A. Rosenheim and G. Jander, *Koll. Zeit.*, **22**. 23, 1918 ; P. E. Browning and H. D. Minnig, *Amer. Journ. Science*, (4), **37**. 72, 1913 ; L. Finckh, *Centr. Min.*, 206, 1902 ; J. O. Perrine, *Phys. Rev.*, (2), **22**. 48, 1923 ; D. D. Karve, *Journ. Indian Chem. Soc.*, **1**. 247, 1925 ; **2**. 128, 1925 ; F. Jirsa, *Zeit. Elektrochem.*, **28**. 186, 1922 ; P. Niggli, *Zeit. Kryst.*, **75**. 228, 1930 ; H. Nisi, *Japan. Journ. Phys.*, **5**. 119, 1929 ; S. Ghosh and N. R. Dhar, *Zeit. anorg. Chem.*, **190**. 421, 1930 ; W. von Behren and J. Traube, *Zeit. phys. Chem.*, **146**. 1, 1930.

§ 11. The Tellurates

What are called the normal tellurates appear as salts of *metatelluric acid*, H_2TeO_4, whilst salts of the *orthotelluric acid*, H_6TeO_6, appear as orthotellurates—*e.g.* Cu_3TeO_6, Ag_6TeO_6, Zn_3TeO_6, and Hg_3TeO_6. There are also salts of the hypothetical *pyrotelluric acid,* $H_2Te_2O_7$; and of the hypothetical *tetratelluric acid,* $H_2Te_4O_{13}$. The normal tellurates, $K_2TeO_4.2H_2O$, $Ag_2TeO_6.2H_2O$, etc., may really be orthotellurates, $K_2H_4TeO_6$ and $Ag_2H_4TeO_6$, respectively.

J. J. Berzelius[1] prepared normal **ammonium tellurate,** $(NH_4)_2.TeO_4$, by the action of solid aq. ammonia on powdered telluric acid; the white glutinous magma dissolves on boiling the mixture, and on cooling the clear soln. becomes turbid, but clarifies as white flakes and granules of this salt are deposited. That which remains in soln. may be precipitated by adding ammonium chloride, and afterwards alcohol. The precipitate is washed with alcohol, which exerts a slight solvent (peptizing) action as the ammonium chloride is washed away. The salt is also obtained by cooling a boiling ammoniacal soln. of normal potassium tellurate in ammonium chloride. F. W. Clarke gave 3·024 for the sp. gr. of the salt at 24·5°, and 3·012, at 25°. J. J. Berzelius said that the white powder dissolves completely in water—slowly if cold, rapidly if boiling. According to A. Gutbier, a boiling aq. soln. of ammonium tellurate—obtained by the action of aq. ammonia on orthotelluric acid—gives a white precipitate with sodium chloride but not with potassium chloride. J. J. Berzelius obtained **ammonium hydrotellurate,** $(NH_4)HTeO_4$, by adding ammonium chloride to a sat. soln. of the corresponding sodium salt. No precipitate is obtained if the potassium salt is employed. The precipitate adheres to the glass as a glutinous mass which dissolves with difficulty in water; and when boiled with water in open vessels, ammonia is evolved. If heated with water in a closed vessel, it partly melts to a white mass which solidifies on cooling, and part dissolves in the water but separates out on cooling. J. J. Berzelius also reported **ammonium hydropyrotellurate,** $(NH_4)HTe_2O_7$, to be formed by adding ammonium chloride to the corresponding sodium salt. The addition of alcohol facilitates the precipitation of the salt which is then washed with alcohol. If a soln. of the hydrotellurate is left to evaporate spontaneously, or by the aid of a gentle heat, the hydropyrotellurate remains as a gummy film. The salt fuses with intumescence when heated, and water is given off. The salt is slightly soluble in water. The colloidal nature of the ammonium tellurates was discussed by A. Rosenheim and G. Jander—*vide infra,* lithium tellurates. C. Ewald made a number of complex organic tellurates.

J. J. Berzelius prepared normal **lithium tellurate,** $Li_2TeO_4.nH_2O$, as a gum-like mass on evaporating the aq. soln. of telluric acid mixed with the required proportion of lithium hydroxide. F. Mylius obtained what was probably **lithium orthotellurate,** $Li_4H_2TeO_6.7H_2O$ by sat. a conc. soln. of orthotelluric acid with lithium hydroxide. The sparingly-soluble salt is hydrolyzed by water. J. J. Berzelius prepared **lithium hydrotellurate,** $LiHTeO_4.nH_2O$, as a gummy mass by evaporating a mixture of telluric acid and lithium hydroxide. A soln. of 4 mols of orthotelluric acid, and a mol of lithium carbonate in water, when spontaneously evaporated yields **lithium hydropyrotellurate,** $LiHTe_2O_7.nH_2O$, which, when heated to 100° forms insoluble **lithium tetratellurate,** $Li_2Te_4O_{13}$. A. Rosenheim and G. Jander showed that the lithium salts behave in many ways like the free acid—(i) they have no definite solubility in water; (ii) the quantity of water which the crystals contain varies according to the conc. of the liquid from which they are deposited; and (iii) they undergo dehydration without any appreciable change in their appearance. In these and other respects the salts resemble colloids—(i) they not only adsorb water, but (ii) the lithium salts and basic salts behave like adsorption compounds of telluric acid and lithium hydroxide.

J. J. Berzelius fused tellurium dioxide with sodium nitrate and obtained a sodium tellurate—*vide* potassium tellurate. According to F. Mylius, what appears to be **sodium dihydrorthotellurate,** $Na_4H_2TeO_6.7H_2O$, was obtained in slender, felted needles by supersaturating a conc. soln. of telluric acid with sodium hydroxide. It is hydrolyzed by water to **sodium tellurate,** $Na_2TeO_4.2H_2O$, which may be **sodium tetrahydrorthotellurate,** $Na_2H_4TeO_6$. This salt was prepared by J. J. Berzelius. He found that the *dihydrate* separates from a soln. of telluric acid in hot soda-lye partly on cooling and partly on the addition of alcohol. It is also obtained by evaporating to dryness, below 100°, a soln. of equimolar parts of telluric acid and sodium carbonate, so as to get rid of all the carbon dioxide, hence, sodium hydroxide is now used instead of the carbonate. The salt was also prepared and analyzed by A. Gutbier. The crystals of the salt do not part with all water until they are nearly at a red-heat. The salt is sparingly soluble in cold and hot water, and it does not separate on cooling the hot soln.; but if sodium hydroxide be added to the soln., the tellurate separates in grains. The evaporation of the aq. soln. on a water-bath leaves a soluble, soft, gummy mass which when dried is but sparingly soluble. F. Mylius said that the salt furnishes doubly refracting six-sided plates; and that at 18°, 100 parts of water dissolve about 0·77 part of salt, and at 100°, about 2·0 parts. R. Funk made some observations on the solubility of the salt. W. G. Mixter gave for the heat of formation $(Na_2O,TeO_3)=124·3$ Cals. A. Miolati and E. Mascetti found that the mol. electrical conductivity, μ, of a mol of Na_2TeO_4 is v litres, at 25°, is

v . .	32	64	128	256	512	1024
μ . .	90·65	94·83	98·33	100·5	103·9	107·6

F. Mylius said that the aq. soln. has an alkaline reaction, and is decomposed by carbon dioxide. E. Blanc calculated the percentage hydrolysis of a $0·0093N$-soln. to be 13·97. J. J. Berzelius added that the salt dehydrated below a red-heat remains white when hot, and dissolves in hot, dil. nitric acid, but in cold or hot water is peptized to a turbid liquid. According to F. Mylius, the *tetrahydrate*, $Na_2TeO_4.4H_2O$, is formed in prismatic crystals from a 30 per cent. soln. of telluric acid sat. with sodium hydroxide. It is more soluble than the dihydrate—100 parts of water dissolve about 1·43 parts of salt at 18°, and at 50°, about 2·5 parts. The salt in contact with water passes into the dihydrate in a few weeks at ordinary temp., and in a few hrs. at 60°. The tetrahydrate recalls the corresponding hydrate of sodium chromate; the *decahydrate* could not be prepared by F. Mylius, or R. Funk. A. Rosenheim and G. Jander made similar observations with respect to the colloidal nature of the sodium tellurates as of the lithium tellurates—*vide supra.*

According to J. J. Berzelius, **sodium hydrotellurate,** $NaHTeO_4.1\frac{1}{2}H_2O$, is obtained by dissolving telluric acid in a boiling soln. of sodium carbonate and adding acetic acid after cooling. The salt first precipitated is redissolved, and when the soln. is evaporated to dryness leaves a mixture of acetate and hydrotellurate—the acetate can be extracted with alcohol. The hydrotellurate is slowly but completely soluble in water, and when the soln. is spontaneously evaporated, it forms a gummy mass, which becomes milk-white when heated, and the product dissolves very slowly in water. When dehydrated by heat the hydrotellurate furnishes a mixture of soluble pyrotellurate and very sparingly soluble tellurate. The hydrotellurate is also produced from a soln. of 2 mols of telluric acid, and a mol of sodium carbonate. E. Blanc found that 0·117 per cent. of the salt is hydrolyzed in a $0·0093N$-soln. A soln. of four mols of orthotelluric acid, and a mol of sodium carbonate furnishes a gummy mass of **sodium hydropyrotellurate,** $NaHTe_2O_7$, when spontaneously evaporated. When heated, it furnishes insoluble **sodium tetratellurate,** $Na_2Te_4O_{13}$.

C. F. Rammelsberg, J. W. Retgers, L. Staudenmaier, and A. Gutbier could not prepare the crystallized, anhydrous **potassium tellurate,** K_2TeO_4, of A. Handl and V. von Lang, isomorphous with potassium sulphate; potassium tellurate shows no inclination to form isomorphous mixtures with potassium sulphate or selenate. J. J. Berzelius obtained the *pentahydrate*, $K_2TeO_4.5H_2O$, from a soln. of telluric acid and potassium hydroxide. The soft, glutinous mass dissolves on the application of a moderate heat, and on cooling the soln. to 0°, the pentahydrate crystallizes out completely provided the alkali-lye is not too dil. The crystals are washed with alcohol. If the alkali-lye is too dilute, the salt does not separate until alcohol is added. If the alcohol is added in small portions at a time, the salt separates in oily drops which afterwards crystallize; if a large quantity of alcohol is added at once, crystals of the salt separate out immediately. The salt was also obtained by J. J. Berzelius by evaporating to dryness a soln. of equimolar parts of telluric acid and potassium carbonate; but E. B. Hutchins added that the process gives a poor result because the telluric acid does not drive out the carbon dioxide from an eq. amount of potassium carbonate. The salt was obtained by the double decomposition of silver tellurate and potassium bromide dissolved in a little warm water, and slowly evaporating the liquid in air free from carbon dioxide. The analyses of A. Gutbier, L. Staudenmaier, J. J. Berzelius, and E. B. Hutchins agree with the formula $K_2TeO_4.5H_2O$; and this salt was found to be produced at ordinary temp. from neutral or slightly alkaline soln. According to J. W. Retgers, with conc. soln. of potassium hydroxide, doubly refracting crystals of the *dihydrate*, $K_2TeO_4.2H_2O$, are produced; and A. Gutbier, and E. B. Hutchins obtained crystals of the dihydrate from a soln. of orthotelluric acid in a boiling, conc. soln. of potassium hydroxide. According to J. J. Berzelius, the pentahydrate furnishes prismatic crystals which, according to L. Staudenmaier, belong to the monoclinic system. J. J. Berzelius found that the pentahydrate when heated gives off water and sinters to a white mass; and A. Gutbier added that at 200°, water and oxygen are given off, and tellurite is formed. According to J. J. Berzelius, when the crystals of the pentahydrate are exposed to air, they become moist without deliquescence forming a mixture of hydrotellurate and carbonate. The salt is soluble in water but not in alcohol. A small proportion of one of the stronger acids added to the aq. soln. precipitates the hydrotellurate; a larger proportion of acid precipitates the pyrotellurate; while a still larger proportion of acid removes all the alkali forming a clear soln. If the acid be acetic acid, the evaporation of the clear soln. furnishes a mixture of potassium acetate and tellurate. A. Rosenheim and G. Jander made similar observations with respect to the colloidal nature of the potassium tellurates as were made in the case of the lithium tellurates—*vide supra.* C. Hugot found that potassium tellurate suspended in dil. hydrochloric acid, and treated with zinc, or suspended in dil. alkali-lye, and treated with aluminium, furnishes tellurium.

According to J. J. Berzelius, **potassium hydrotellurate,** $KHTeO_4.1\frac{1}{2}H_2O$, is formed from a soln. of the correct proportion of potassium carbonate in orthotelluric acid evaporated at ordinary temp.; by cooling a boiling soln. of 2 mols of orthotelluric acid and a mol of potassium carbonate; while the exposure of a soln. of the normal tellurate to air results in the deposition of the hydrotellurate, and, added E. B. Hutchins, this salt is precipitated on passing carbon dioxide into an aq. soln. of the normal salt—an excess of the carbon dioxide does no harm. J. J. Berzelius also obtained the hydrotellurate by evaporating to dryness a soln. of the normal tellurate in acetic acid, and washing out the acetate with alcohol of sp. gr. 0·85. He also obtained the salt by fusing tellurium dioxide with potassium nitrate to a clear liquid; digesting the cold mass with boiling water to remove nitrites and nitrates; and dissolving the residue in boiling water—it does not dissolve in water holding nitrate in soln. When the hot soln. is cooled, crystals of the hydrotellurate are deposited. The higher the fusion temp. the greater the proportion of tellurite mixed with the tellurate. This process, added J. J. Berzelius, sometimes yields a product which is insoluble in boiling water, acids, or soln. of alkalies; it is white when cold, yellow when hot, and when heated fuses giving off oxygen and forming potassium pyrotellurite. E. B. Hutchins' analysis of the hydrotellurate corresponds with $K_2O.2TeO_3.4H_2O$. The salt has an alkaline reaction, and it has a metallic, slightly alkaline taste. When heated, it gives off water, turns yellow, and at a higher temp.—below redness—fuses forming normal tellurate and tetratellurate: $6KHTeO_4=2K_2TeO_4+K_2Te_4O_{13}+3H_2O$—the tellurate can be extracted by water. The hydrotellurate is sparingly soluble in cold water, but more soluble in hot water.

J. J. Berzelius prepared **potassium hydropyrotellurate,** $KHTe_2O_7.1\frac{1}{2}H_2O$, by slowly cooling a boiling soln. of 4 mols of orthotelluric acid and a mol of potassium carbonate. E. B. Hutchins' analysis agree with $K_2O.4TeO_3.4H_2O$. J. J. Berzelius found that this salt is precipitated when nitric acid is added to an aq. soln. of the normal tellurate: and, as indicated above, it is formed by adding nitric acid to the aq. soln. obtained as above by fusing tellurium dioxide and potassium nitrate. The white, pulverulent salt loses 7·5 per cent. of water at a gentle heat, but retains 0·15 per cent.; it then turns yellow and forms the tetratellurate; and at a higher temp., it gives off 7·71 per cent. of oxygen leaving potassium tellurite behind. The salt is slightly soluble in water; when crystallized from its aq. soln., some hydrotellurate is formed; if the water contains other salts in soln., this decomposition does not occur. E. B. Hutchins prepared **potassium tritellurate,** $K_2Te_3O_{10}.5H_2O$, by evaporating a soln. of a mol of potassium carbonate, and 4 mols of telluric acid. It furnishes a white, granular mass which is much more soluble in hot than in cold water; the aq. soln. has an alkaline reaction. J. J. Berzelius prepared **potassium tetratellurate,** $K_2Te_4O_{13}$, by calcining the hydropyrotellurate; by very gently heating tellurium dioxide with potassium chlorate, and extracting the product with water to remove potassium chloride and chlorate; by the action of chlorine on a hot soln. of potassium tellurite, and washing the product with water; and also by heating orthotelluric acid with potassium nitrate and chloride below redness, and washing with water. The yellow powder is insoluble at ordinary temp. in water, dil. mineral acids, and potash-lye; it slowly dissolves in boiling nitric acid, and rapidly in molten potash-lye.

J. F. Norris and W. A. Kingman prepared **rubidium tellurate,** $Rb_2TeO_4.3H_2O$, by evaporating in vacuo over sulphuric acid, a soln. of orthotelluric acid mixed with a 25 per cent. excess of rubidium hydroxide. The colourless prisms with pyramidal ends dissolve in ten times their weight of water. The salt is decomposed by carbon dioxide so that it cannot be made from orthotelluric acid and rubidium carbonate. If a soln. of rubidium carbonate and telluric acid in calculated quantities be evaporated, **rubidium hydrotellurate,** $RbHTeO_4.\frac{1}{2}H_2O$, is formed. It is not isomorphous with the corresponding hydroselenate; 100 parts of cold water dissolve about 5 parts of the salt; the salt is more soluble in hot water. G. Pellini mixed nearly sat. aq. soln. of rubidium hydrotellurate and hydroselenate, in various proportions, and on evaporating the mixed soln. at 50°–80° until they deposited crystals on cooling, obtained mixed crystals of the two salts containing from 42 to 53 mols. per cent. of the selenate. With soln. still richer in selenate, crystals containing up to 100 per cent. selenate can be obtained. There is, however, a limit to the proportion of tellurate in the mixed crystals since all soln. containing more than about 50 molar per cent. of the tellurate deposit the latter in the pure state. With mixed soln. of rubidium hydrosulphate and hydrotellurate, the results can be interpreted on the assumption that a complex salt, $RbHSO_4.RbHTeO_4$, is formed; but there is also a tendency to form solid soln. J. F. Norris and W. A. Kingman prepared by an analogous process, **cæsium hydrotellurate,** $CsHTeO_4.\frac{1}{2}H_2O$, which is produced in small cubic crystals, less soluble than those of the rubidium salt—100 parts of water dissolve about 3·33 parts of the salt.

J. J. Berzelius described the green flocculent precipitate obtained by mixing soln. of potassium tellurate and copper nitrate as normal **copper tellurate,** $CuTeO_4$. E. B. Hutchins showed that if the precipitate be boiled for some hours with water, it forms **copper orthotellurate,** Cu_3TeO_6, which settles as a heavy green powder. It is insoluble in water but soluble in aq. ammonia, a soln. of potassium cyanide, and in acetic, hydrochloric, or nitric acid. No success attended the attempt to obtain the tellurate in a crystalline form by allowing the precipitate to remain in the mother-liquor for weeks; or by allowing copper hydroxide to stand for weeks in contact with an excess of telluric acid.

J. J. Berzelius obtained normal **silver tellurate,** Ag_2TeO_4, in dark yellow, bulky flakes on adding a conc. soln. of silver nitrate to one of normal potassium tellurate. E. B. Hutchins could not prepare the salt in this way, he always obtained a basic salt, and by using potassium hydrotellurate, he obtained a precipitate containing an excess of telluric acid; and, as observed by A. Gutbier, the product is decomposed into the basic salt by washing. E. B. Hutchins obtained crystals of the *dihydrate*, $Ag_2TeO_4.2H_2O$, which may be **silver tetrahydrorthotellurate,** $Ag_2H_4TeO_6$, by treating silver oxide with an excess of a soln. of telluric acid; by mixing a soln. of 20 grms. of silver acetate, acidified with a few drops of acetic acid, with a soln. of 1·4 grms. of telluric acid, and evaporating the soln. at room temp. in darkness; and by adding a silver nitrate soln. to a conc. soln. of potassium tellurate containing an excess of acetic acid, and allowing the yellow or brown precipitate to stand for some hours in contact with the mother-liquid. Owing to their greater sp. gr., the crystals can be easily separated from the amorphous salt. The straw-yellow crystals are rhombic bipyramids with the axial ratios $a : b : c = 0·722 : 1 : 2·107$, and they are isomorphous with the corresponding sulphate and selenate. The crystals are slowly darkened in light; and when heated to 200°, they lose water and become black; at a higher temp. oxygen is evolved and a greyish-brown, fusible mass remains. The salt is insoluble in hot or cold water, but soluble in aq. ammonia, an aq. soln. of potassium cyanide, or sodium thiosulphate, and in nitric, sulphuric, and acetic acids. Conc. acids decompose the salt completely forming telluric acid and the corresponding silver salt. J. J. Berzelius said that by mixing an ammoniacal soln. of silver tellurate with ammoniacal silver nitrate, and evaporating, the basic salt, **silver dioxytellurate,** $2Ag_2O.Ag_2TeO_4$, or possibly **silver orthotellurate,** Ag_6TeO_6, is formed; and the same product is obtained by treating a dil. soln. of silver nitrate with potassium tellurate. The reddish-yellow precipitate soon blackens. J. J. Berzelius also prepared **silver oxyditellurate,** $Ag_2O.2Ag_2TeO_4$, or $Ag_6Te_2O_9$, as a brown powder by boiling silver nitrate with water. E. B. Hutchins said that if the crystals of dihydrated silver tellurate are allowed to stand in contact with a cold soln. of a silver salt, red monoclinic crystals of the *trihydrate*, $Ag_6Te_2O_9.3H_2O$, are formed. They are not changed by cold water, but with boiling water a brown mass is formed. In sunlight the crystals become opaque and copper-red. If heated over 110°, the salt loses water and becomes black; all the combined water is expelled at 200°. J. J. Berzelius said that by double decomposition with silver nitrate and potassium hydrotellurate, **silver hydrotellurate,** $AgHTeO_4$, is formed; likewise also **silver tetratellurate,** $Ag_2Te_4O_{13}$; but E. B. Hutchins could obtain neither of these salts.

E. B. Hutchins did not succeed in making **gold tellurate.** If gold chloride be added to normal silver tellurate suspended in water, silver chloride and gold oxide are precipitated; and the evaporation over sulphuric acid of a mixed soln. of potassium tellurate and gold chloride furnishes yellow crystals of potassium chloroaurate.

J. J. Berzelius prepared **calcium tellurate,** $CaTeO_4$, by precipitation. The white flecks dissolve in hot water, and the evaporation of the soln. yields a white powder; **strontium tellurate** was obtained in an analogous manner; and **barium tellurate,** $BaTeO_4.3H_2O$, appears as a voluminous, white precipitate when a soln. of barium chloride is treated with sodium tellurate. The precipitate soon forms a heavy, white powder. It loses its water of crystallization when heated over 200°. F. C. Mathers and G. M. Bradbury found that when tellurium dioxide is mixed with 5 eq. of tellurium dioxide, and heated for an hour at 975°, almost the theoretical yield of calcium tellurate is formed. At a lower temp. the yield was smaller. F. W. Clarke gave 4·55 for the sp. gr. of anhydrous barium tellurate at 10·5°; 4·53 at 10°; and 4·48 at 16°; when dried at 200°, the sp. gr. is 4·2. J. J. Berzelius found that barium tellurate is sparingly soluble in cold water, and rather more soluble in hot water. When the aq. soln. is evaporated a white earth remains. It is not decomposed by ammonia; and it is soluble in hydrochloric and nitric acids. If sodium hydrotellurate be added to a soln. of barium chloride a voluminous precipitate of **barium hydrotellurate,** $Ba(HTeO_4)_2.2H_2O$, was obtained. It is resolved by water into a soluble acid salt, and into the normal tellurate. Sodium hydropyrotellurate precipitates **barium hydropyrotellurate,** $Ba(HTe_2O_7)_2.nH_2O$, from a soln. of barium chloride. The voluminous precipitate is easily soluble in water; and in acetic acid. It is yellow when hot, white when cold.

J. J. Berzelius obtained **beryllium tellurate** as a white, voluminous precipitate by double decomposition with a soluble tellurate and a beryllium salt; and **magnesium tellurate** in an analogous manner. Magnesium tellurate is more soluble than the corresponding salts of the alkaline earths. Sodium hydrotellurate precipitates from a soln. of a magnesium salt, **magnesium hydrotellurate,** which is more soluble than the normal tellurate. A. Gutbier prepared **zinc tellurate** as a white, insoluble precipitate by mixing soln. of potassium tellurate and zinc chloride. E. B. Hutchins showed that the precipitate obtained with soln. of zinc nitrate and potassium tellurate becomes heavy and granular when treated with hot water. Its composition is Zn_3TeO_6; it is insoluble in water, but soluble in acetic, nitric, hydrochloric, and sulphuric acids. A. Oppenheim obtained **cadmium tellurate** as an insoluble white precipitate on treating cadmium nitrate with sodium tellurate. It forms a colourless soln. with hydrochloric acid.

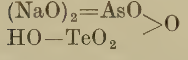
J. J. Berzelius noticed that when powdered crystalline mercurous nitrate is immersed in an aq. soln. of potassium hydrotellurate, a dark brown precipitate is formed; and a yellowish-brown precipitate of **mercurous tellurate,** Hg_2TeO_4, is produced by the action of potassium tellurate on a soln. of mercurous nitrate. G. Denigès also obtained this salt in a similar way. J. J. Berzelius said that mercurous tellurate soon becomes yellow, owing to the action of the free acid in the liquid probably forming mercurous hydrotellurate, $HgHTeO_4$. Crystals of the normal mercurous tellurate have not been prepared. F. A. Genth discovered radiating tufts of minute, acicular or capillary, white crystals as a decomposition product of coloradoite in a mine in the Magnolia district, Colorado; and he called the mineral **magnolite.** He inferred that its composition is mercurous tellurate, Hg_2TeO_4, since it behaves towards hydrochloric acid somewhat as represented by the equation: $Hg_2TeO_4+8HCl=2HgCl_2+TeCl_4+4H_2O$. It is blackened by aq. ammonia, and is soluble in dil. nitric acid. E. B. Hutchins found that when a large excess of a cold conc. soln. of potassium tellurate is added to a conc. soln. of mercurous nitrate the yellow precipitate, which is first formed, quickly changes to a brown. The precipitate is slimy and difficult to wash. It approximates Hg_2TeO_4 in composition. E. B. Hutchins was unable to prepare **mercurous orthotellurate,** Hg_6TeO_6. When the bulky yellow precipitate, obtained by treating a hot dil. soln. of potassium tellurate with an excess of mercurous nitrate soln., is washed with hot water and boiled for some time in water it is decomposed, giving free mercury. The precipitate may be boiled for several hours without changing in appearance, but at length it settles as a heavy, brown granular powder containing free mercury. This change may be hastened by rubbing some of the precipitate against the side of the beaker with a glass rod. When the brown powder is heated with hydrochloric acid, elementary tellurium is precipitated. A. Oppenheim obtained mercurous tellurate by the action of telluric acid on a soln. of mercurous nitrate. E. B. Hutchins showed that if an excess of mercurous nitrate is employed with a hot dil. soln. of potassium tellurate, a yellow, amorphous, basic salt, **mercurous oxyditellurate,** $Hg_2O.2HgTeO_4$, is formed. A basic salt was also prepared by F. Teltscher. E. B. Hutchins found that when conc. soln. of mercurous nitrate and a soluble tellurate or telluric acid are mixed, the precipitate may vary in composition from the basic salt just indicated to **mercurous hydrotellurate,** $HgHTeO_4$, any precipitate of mercurous tellurate may be changed to crystals of the hydrotellurate by treatment with a cold conc. soln. of telluric acid. This acid tellurate is not only the only crystalline mercurous tellurate that has been prepared, but it is the only mercurous tellurate of definite composition that has been obtained. Mercurous tellurate is a striking example of a salt of a weak acid and a weak base. Slight variations of the conditions under which a salt is placed may bring about a change in its composition, causing it to become either more acid or more basic. This, together with the fact that the salt is readily decomposed giving free mercury and mercuric tellurate, renders the preparation of the mercurous tellurates somewhat difficult. The *trihydrate*, $HgHTeO_4.3H_2O$, may be conveniently prepared by treating a soln. of mercurous nitrate with telluric acid and subsequent change of the precipitate to the crystalline salt. When the soln. of telluric acid is added to a soln. of mercurous nitrate a bright yellow precipitate is formed. If a large excess of telluric acid is added, the yellow precipitate becomes nearly white and slowly changes to colourless crystals of $HgTeO_4.3H_2O$. The presence of considerable free nitric acid in the soln. aids greatly in the formation of crystals of the salt. Under these conditions crystals frequently form on the walls of the containing vessel. F. Teltscher found that the potential of platinized platinum in water with mercurous tellurate, $Hg_2TeO_4.6HgO.6H_2O$, in suspension, is —1·025 volt in darkness, and —0·1000 volt in light; if $0{\cdot}25N$-H_2TeO_4 is used in place of water, the values are respectively —0·93 and —0·96 volt; and with N-H_2TeO_4, —0·93 and —0·94 volt.

J. J. Berzelius, F. Teltscher, and E. B. Hutchins prepared **mercuric tellurate,** $HgTeO_4$, as a white, flocculent precipitate by mixing conc. soln. of mercuric nitrate and potassium tellurate or telluric acid at 0°. E. B. Hutchins found that the precipitate is quickly decomposed by water at room temp. into telluric acid and basic mercuric tellurate. This decomposition goes on even when the precipitate is washed with water at 0°: consequently it is impossible to obtain a pure white product in suitable condition for analysis. The precipitate remains white indefinitely in a sat. soln. of telluric acid at room temp. Crystals of the *dihydrate*, $HgTeO_4.2H_2O$, free from the basic salt were obtained by mixing conc. soln. of telluric acid and mercuric nitrate at 0° and allowing the resulting soln. to stand at room temp. until the salt crystallized out. The dihydrate appears as transparent crystals belonging to the orthorhombic system. It is slowly decomposed by cold water. Boiling water quickly decomposes it into telluric acid and basic mercuric tellurate. If the white precipitate of mercuric tellurate formed by mixing conc. soln. of mercuric nitrate and potassium tellurate containing free nitric acid, is allowed to remain undisturbed in the mother-liquor for several days at room temp., nearly all of it is converted into crystalline **mercuric orthotellurate,** Hg_3TeO_6, corresponding with turpeth mineral, Hg_3SO_6. Indeed, all precipitates of mercuric tellurate, whether crystalline or amorphous, show a strong tendency to change to mercuric orthotellurate in the presence of water. This property of mercuric tellurate renders it difficult to prepare the salt $HgTeO_4$ in pure condition. When an excess of mercuric nitrate is added to a hot dil. soln. of potassium tellurate, a heavy, yellow granular precipitate of mercuric orthotellurate is formed. If a cold, conc. soln. of mercuric nitrate is added to a conc. soln. of potassium tellurate made acid with nitric acid, a white flocculent precipitate of $HgTeO_4$ is formed. At room temp. a portion of the precipitate usually assumes a yellow colour immediately, probably due to the formation of a basic salt. If the acid soln. containing this white or yellow flocculent precipitate is allowed to stand undisturbed for several days the precipitate is largely converted into transparent amber-coloured crystals of the orthotellurate. Frequently the walls of the containing vessel are covered with crystals that have separated from the acid soln. In many cases the amber-coloured crystals form in contact with the white amorphous precipitate, but in all cases the crystals are entirely distinct from the precipitate. Mercuric orthotellurate crystallizes in the cubic system, the predominating form being the dodecahedron. Combinations of the cube and dodecahedron are frequent, while many crystals show a broad octahedral face on which the crystal has grown. The crystals contain a little nitric acid and about 0·6 per cent. of water. This is considerably less than one-half of a mol of water to one of Hg_3TeO_6. When heated, the salt assumes a red colour, but it regains its original colour upon cooling. The crystals are not altered by heating to 140°. The crystals are insoluble in water and unchanged by boiling with water. They are soluble in nitric acid but more readily soluble in hydrochloric acid. W. von Behren and J. Traube studied the stability of the colloidal soln. of the tellurate, $Hg_3H_3TeO_6$. F. Teltscher stated that he had obtained a basic *mercuric tellurate*, $Hg_2O.6HgO.TeO_3.6H_2O$, by the action of a conc. soln. of mercurous nitrate on a soln. of telluric acid. The yellow precipitate can be kept a long time in darkness without change, but it blackens in daylight.

J. J. Berzelius prepared **aluminium tellurate** as a white precipitate by the action of a soluble tellurate on a soln. of an aluminium salt. The precipitate is soluble in an excess of the aluminium salt. A. Oppenheim was unable to prepare *potassium aluminium tellurate* analogous to the alums. F. W. Clarke prepared **thallous tellurate,** Tl_2TeO_4, by mixing soln. of ammonium tellurate and thallous nitrate. The heavy, white precipitate recalls that of silver chloride. L. M. Dennis and M. Doan also obtained it as a white flocculent precipitate, sparingly soluble in water, by mixing soln. of telluric acid and thallous hydroxide. F. W. Clarke found that when dried at 120°, its sp. gr. is 5·712 at 20°; and 5·687 at 22°. When heated to 180°, the salt becomes pale yellow with the loss of 1·46 per cent. of water, and its sp. gr. is then 6·742 at 16°, and 6·760 at 17·6°. It melts at a red-heat and is reduced to telluride. When hot the colour is black, but on cooling it forms a clear, lemon-yellow glass. J. J. Berzelius obtained **yttrium tellurate** by a method analogous to that used for the aluminium salt. A. Gutbier mixed aq. soln. of telluric acid or an alkali tellurate with an aq. soln. of ammonium cerium nitrate, and obtained a pale yellow, slimy precipitate of **cerous tellurate.** J. J. Berzelius prepared **zirconium tellurate** as a voluminous, white precipitate on mixing soln. of zirconium chloride and sodium hydrotellurate: the precipitate is soluble in an excess of the zirconium salt; likewise also with thorium tellurate which is insoluble in an excess of the thorium salt. A. Gutbier also obtained **thorium tellurate,** as a white, curdy precipitate, from a soln. of potassium tellurate and thorium nitrate.

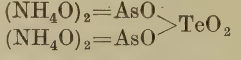
I. Domeyko mentioned the occurrence of lead tellurate in a mine in the province of Coquimbo, Chile. J. J. Berzelius said that a basic salt is produced as a voluminous, white precipitate when potassium hydrotellurate and basic lead acetate soln. are mixed; he obtained **lead tellurate,** $PbTeO_4$, by mixing soln. of normal lead acetate and potassium tellurate; the white, heavy precipitate is sparingly soluble in water; by the use of alkali hydrotellurate, **lead hydrotellurate,** $Pb(HTeO_4)_2.nH_2O$, is formed, and it is more soluble in water than the normal tellurate. F. C. Mathers and F. V. Graham obtained lead tellurate by the action of lead dioxide on tellurium dioxide at 170°. According to J. J. Berzelius, a precipitate of **lead tetratellurate,** $PbTe_4O_{13}$, is produced when an alkali tetratellurate is used as precipitant. It is yellow when hot, and white when cold. It is soluble in dil. nitric acid, even after ignition; less soluble in acetic acid; and fairly soluble in water.

A. Oppenheim was unable to prepare an **arsenic tellurate.** According to R. F. Weinland and H. Prause, telluric acid unites with the arsenates of the alkali metals to form complex salts. Thus, **ammonium diarsenatotellurate,** $2(NH_4)_2O.As_2O_5.TeO_3.4H_2O$, was obtained by adding 4 mols of aq. ammonia to a soln. of orthotelluric acid and 4 mols of ammonium dihydroarsenate, in as little water as possible, at ordinary temp., and evaporating the soln. over sulphuric acid. The triclinic crystals are isomorphous with the corresponding phosphate, and have the axial ratios $a:b:c=0·7241:1:0·7468$, and $\alpha=90° 34'$, $\beta=94° 7'$, and $\gamma=92° 17'$. Likewise **ammonium triarsenatotellurate,** $4(NH_4)_2O.3As_2O_5.2TeO_3.11H_2O$, was obtained using a mol of orthotelluric acid, 4 mols of ammonium dihydroarsenate, and a mol of ammonia. The crystals are isomorphous with the corresponding phosphate. Similarly, using a mol of orthotelluric acid, 4 mols of arsenic acid, and 5·2 mols of sodium hydroxide, **sodium arsenatotellurate,** $2Na_2O.As_2O_2.2TeO_3.9H_2O$, was obtained in small, six-sided plates. *Potassium and rubidium arsenatotellurates* could not be prepared. The graphic formulæ given for the above salts are:



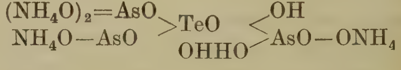
$$\begin{matrix}(NaO)_2{=}AsO \\ HO{-}TeO_2\end{matrix}\!>\!O$$

$2Na_2O.As_2O_5.2TeO_3.9H_2O$



$$\begin{matrix}(NH_4O)_2{=}AsO \\ (NH_4O)_2{=}AsO\end{matrix}\!>\!TeO_2$$

$2(NH_4)_2O.As_2O_5.TeO_3.4H_2O$



$$\begin{matrix}(NH_4O)_2{=}AsO \\ NH_4O{-}AsO\end{matrix}\!>\!\begin{matrix}TeO \\ OHHO\end{matrix}\!<\!\begin{matrix}OH \\ AsO{-}ONH_4\end{matrix}$$

$4(NH_4)_2O.3As_2O_5$

A. Oppenheim could not prepare *antimony tellurate.* F. A. Genth found a yellowish-, greenish- or brownish-red, soft, earthy incrustation, without distinct crystalline structure on the tetradymite of Highland, Montana, and he called the mineral **montanite ;** it was also found by T. W. E. David to accompany the tetradymite of Norongo, New South Wales. Analyses reported by F. A. Genth, T. W. E. David, and C. F. Rammelsberg, agree with $Bi_2O_3.TeO_3.2H_2O$, or $Bi_2O_3.TeO_3.H_2O$. It can therefore be regarded as a hydrated **bismuth orthotellurate,** $Bi_2TeO_6.2H_2O$, hydrated **bismuthyl tellurate,** $(BiO)_2TeO_4.H_2O$, or, according to P. Groth and K. Mieleitner, $\{Bi(OH)_2\}_2TeO_4$.

J. J. Berzelius prepared **chromic tellurate** in greyish-green flecks by mixing soln. of a chromic salt and an alkali tellurate. It is soluble in an excess of a chromic salt soln., but not in soln. of potassium tellurate or sulphate. A. Oppenheim also prepared this salt, but he was unable to obtain *potassium chromium tellurate* analogous to chrome-alum. A. Berg evaporated spontaneously an aq. soln. containing 2 mols of chromium trioxide and a mol each of potassium dichromate and telluric acid. An ill-defined crystalline crust of **potassium chromotellurate,** $2K_2O.4CrO_3.TeO_3$, was obtained ; similarly with **ammonium chromotellurate,** $2(NH_4)_2O.4CrO_3.TeO_3$; and the very soluble **sodium chromotellurate,** $2Na_2O.4CrO_3.TeO_3$. He regarded these salts as derivatives of **chromotelluric acid,** $TeO(O.CrO_2.OH)_4$, which, in turn, is derived from *paratelluric acid,* $TeO(HO)_4$.

V. W. Meloche and W. Woodstock obtained **ammonium telluratohexamolybdate,** $3(NH_4)_2O.TeO_3.6MoO_3.7H_2O$, from a soln. of a mol of telluric acid and 4 mols of molybdic acid with enough aq. ammonia to satisfy the telluric acid, by evaporation and crystallization. A soln. of equimolar proportions of telluric and molybdic acids, with enough ammonia to satisfy half the hydrogen atoms of telluric acid, H_2TeO_6, on evaporation and cooling, gave clear, white crystals of **ammonium ditelluratohexamolybdate,** $3(NH_4)_2O.2TeO_3.6MoO_3.10H_2O$. Both compounds decompose at 550° leaving a residue of tellurium dioxide with a small amount of molybdic acid.

J. J. Berzelius similarly prepared **uranyl tellurate** as a voluminous pale yellow precipitate insoluble in an excess of uranyl nitrate soln. A. Gutbier found it to be readily soluble in cold hydrochloric acid. J. O. Perrine said that it shows no ultra-violet fluorescence with the X-rays.

J. J. Berzelius obtained **manganese tellurate** as a white flocculent precipitate by mixing soln. of alkali tellurate and a manganese salt. J. J. Berzelius obtained **ferric tellurate** in pale yellow flakes soluble in an excess of the ferric salt ; and **ferrous tellurate** as a white precipitate, which, on exposure to air, becomes greenish-grey and then brownish-red. F. A. Genth reported a straw-yellow to greenish-yellow mineral which he called **ferrotellurite** occurring at the Keystone Mine, Magnolia District, Colorado. It was supposed to be ferrous tellurate, $FeTeO_4$, but, according to J. D. Dana, the crystals may have been those of tellurite coloured with ferric oxide. The mineral was insoluble in aq. ammonia ; and soluble in hydrochloric acid. J. J. Berzelius obtained **cobalt tellurate,** as a voluminous bluish-purple precipitate, and **nickel tellurate** as a pale green precipitate.

J. F. Norris and H. Fay could not prepare any **tellurothionates** analogous to selenotetrathionate.

REFERENCES.

[1] J. J. Berzelius, *Schweigger's Journ.*, **6**. 311, 1812 ; **34**. 78, 1823 ; *Pogg. Ann.*, **28**. 392, 1833 ; **32**. 1, 577, 1834 ; F. W. Clarke, *Amer. Journ. Science*, (3), **14**. 286, 1877 ; (3), **16**. 401, 1878 ; W. G. Mixter, *ib.*, (4), **29**. 488, 1910 ; A. Gutbier, *Studien über das Tellur*, Leipzig, 1901 ; *Zeit. anorg. Chem.*, **31**. 342, 1901 ; A. Gutbier and F. Flury, *ib.*, **32**. 272, 1902 ; V. W. Meloche and W. Woodstock, *Journ. Amer. Chem. Soc.*, **51**. 171, 1929 ; F. C. Mathers and F. V. Graham, *ib.*, **51**, 3225, 1929 ; F. C. Mathers and G. M. Bradbury, *ib.*, **51**. 3229, 1929 ; A. Berg, *Compt. Rend.*, **152**. 1587, 1911 ; *Bull. Soc. Chim.*, (4), **9**. 583, 1911 ; C. Hugot, *ib.*, (4), **27**. 33, 1920 ; (4), **29**. 1070, 1921 ; F. Mylius, *Ber.*, **34**. 2209, 1901 ; R. Funk, *ib.*, **33**. 3696, 1900 ; C. Ewald, *Studien über das Tellur, Beiträge zur Kenntnis der Hexahalogenotellureate*, Erlangen, 1912 ; E. B. Hutchins, *Journ. Amer. Chem. Soc.*, **27**. 1157, 1905 ; L. M. Dennis and M. Doan, *ib.*, **18**. 975, 1896 ;

L. Michel, *Recherches sur quelques tungstates, molybdates, séléniates, tellurates cristallisés*, Paris, 1889; L. Staudenmaier, *Untersuchungen über das Tellur*, Leipzig, 1895; *Zeit. anorg. Chem.*, **10**. 197, 1895; A. Oppenheim, *Beobachtungen über das Tellur und einige seiner Verbindungen*, Göttingen, 1959; *Journ. prakt. Chem.*, (1), **71**. 278, 1857; A. Handl and V. von Lang, *Sitzber. Akad. Wien*, **43**. 117, 1861; J. D. Dana, *A System of Mineralogy*, New York, 989, 1892; P. Groth and K. Mieleitner, *Mineralogische Tabellen*, München, 51, 1921; C. F. Rammelsberg, *Handbuch der krystallographischphysikalischen Chemie*, Leipzig, **1**. 606, 1881; *Handbuch der Mineralchemie*, Leipzig, 375, 1875; **2**. 182, 1895; J. W. Retgers, *Zeit. phys. Chem.*, **10**. 536, 1892; A. Miolati and E. Mascetti, *Gazz. Chim. Ital.*, **31**. i, 93, 1901; G. Pellini, *Atti Accad. Lincei*, (5), **15**. i, 629, 711, 1900; (5), **18**. ii, 279, 1909; E. Blanc, *Journ. Chim. Phys.*, **18**. 28, 1920; J. F. Norris and W. A. Kingman, *Amer. Chem. Journ.*, **26**. 318, 1901; J. F. Norris and H. Fay, *ib.*, **23**. 119, 1900; F. A. Genth, *Proc. Amer. Phil. Soc.*, **17**. 118, 1877; *Amer. Journ. Science*, (2), **45**. 318, 1868; F. Teltscher, *Ueber das elektrometrische Verhalten von Quecksilbersalzlösungen*, München, 51, 1912; J. O. Perrine, *Phys. Rev.*, (2), **22**. 48, 1923; I. Domeyko, *Compt. Rend.*, **81**. 632, 1875; H. Prause, *Ueber Verbindungen der Tellursäure mit Jodaten, Phosphaten und Arsenaten*, Leipzig, 1901; R. F. Weinland and H. Prause, *Ber.*, **33**. 1015, 1900; *Zeit. anorg. Chem.*, **28**. 45, 1901; T. W. E. David, *Rec. N.S.W. Geol. Sur.*, **1**. 28, 1891; G. Jander, *Ueber die Tellursäure und ihre Alkalisalze in ihrem Verhalten als Halbkolloide*, Berlin, 1917; A. Rosenheim and G. Jander, *Koll. Zeit.*, **22**. 23, 1918; W. von Behren and J. Traube, *Zeit. phys. Chem.*, **146**. 1, 1930; G. Denigès, *Ann. Chim. Anal.*, **20**. 57, 1915.

§ 12. Tellurium Halides

H. Moissan[1] found that powdered tellurium put in contact with fluorine combines with incandescence giving an abundance of white fumes. The whole mass is quickly covered with a solid, crystalline fluoride, easily volatile and very hygroscopic, having the aspect and properties of the **tellurium tetrafluoride,** TeF_4, described by J. J. Berzelius; but E. B. R. Prideaux showed that the product is the hexafluoride—*vide infra*. J. J. Berzelius prepared the tetrafluoride by dissolving tellurium dioxide in hydrofluoric acid, evaporating the liquid on a water-bath to a transparent, colourless syrup which, on cooling, solidified to a milk-white mass of small, warty granules. When the product is heated, water and hydrofluoric acid are given off, and finally a sublimate of tellurium tetrafluoride—an oxyfluoride remains as a residue. R. Metzner treated the mother-liquor, used in the preparation of the oxyfluoride, $TeOF_2.H_2O$, with liquid hydrogen fluoride, cooled to —70°; on raising the temp. to —28°, the liquid portion is removed, and there remain crystals of the tetrafluoride which can be dried on paper at —30°. E. B. R. Prideaux and J. O'Neil Millott did not observe this separation of the tetrafluoride. A *tetrahydrate*, $TeF_4.4H_2O$, was prepared by A. J. Högbom.

A number of **fluotellurites** has been prepared from soln. of tellurous acid and various hydroxides and carbonates in hydrofluoric acid. Thus, H. L. Wells and J. M. Willis prepared **cæsium pentafluotellurite,** $CsTeF_5$, from mixed soln. of tellurium dioxide and cæsium fluoride in hydrofluoric acid. The salt forms transparent, colourless needles. It is decomposed by water; but it is stable in hydrofluoric acid soln. A. J. Högbom prepared **ammonium pentafluotellurite,** $NH_4TeF_5.H_2O$, which furnishes colourless prismatic crystals; **potassium pentafluotellurite,** $KTeF_5$, gives long colourless needles; and **barium pentafluotellurite,** $Ba(TeF_5)_2.H_2O$, gives irregular lamellæ. The crystals become opaque when exposed to air; and are decomposed by water. The fluotellurites of copper, silver, beryllium, and nickel could not be prepared. J. J. Berzelius described **sodium fluotellurite** as a compound which formed ill-defined crystals soluble in a small proportion of boiling water, but decomposed by a larger proportion of water. R. F. Weinland and J. Alfa could not prepare this salt.

E. B. R. Prideaux found that when fluorine acts on tellurium at —78°, white, crystalline **tellurium hexafluoride,** TeF_6, is formed. This melts to a clear, mobile liquid as the temp. rises, and then assumes the gaseous state. The gas has an unpleasant odour recalling that of tellurium hydride and that of ozone. The sp. gr. of the liquid is 3·025 at —35·5°; and the mol. vol., 79·9. The coeff. of expansion of the liquid between —3·5° and 51·5° is 0·032. The m.p. is —36°; and the b.p., —35·5°. The vap. press. of the solid at 35·5° is 760 mm. The critical temp. is 83·25°. The vap. density (oxygen 16) is 119·5, in agreement with a mol. wt. 239 when the calculated value for TeF_3 is 241·6. The refractive index is 1·00091 when the value calculated from the addition rule is 1·001823. The gas does not attack glass; and it is decomposed by water: $TeF_6+4H_2O=H_2TeO_4+6HF$. N. V. Sidgwick discussed this reaction.

The action of chlorine on tellurium has been previously discussed. H. Rose[2] observed that when a slow current of chlorine is passed over strongly heated tellurium, or natural silver telluride, **tellurium dichloride,** $TeCl_2$, accompanied by some tetrachloride, collects as a distillate. The two can be separated by fractional distillation. According to V. Lenher, the dichloride can be prepared by passing the vapour of sulphur monochloride over strongly heated tellurium: $Te+S_2Cl_2=TeCl_2+2S$; the black dichloride soon changes to the white tetrachloride: $TeCl_2+S_2Cl_2=TeCl_4+2S$. K. Lindner and L. Apolant obtained the dichloride by heating tellurium in the vapour of carbonyl chloride; the brown vapours condense to a black crystalline mass. M. Damiens observed no evidence of the existence of the dichloride on the f.p. curve of mixtures of the constituent elements, Fig. 43. Hence, the dichloride is stable only in the gaseous state or in soln. and in equilibrium with its decomposition products—tellurium and tellurium tetrachloride. As it solidifies, it dissociates into a solid soln. of the element in the tetrachloride. J. J. Berzelius, and A. Michaelis heated the mixed di- and tetrachlorides with tellurium in a flask fitted with a reflux condenser for a long time so as to reduce the tetrachloride to the dichloride. Tellurium dichloride is a black, amorphous, hygroscopic solid, which, said H. Rose, does not fume in air; when powdered, it is yellowish-green. A. Michaelis found the vap. density at 444° to be 6·6 to 7·0 (air unity) when the calculated value for $TeCl_2$ is 6·89. A. Michaelis gave 175° for the m.p., and T. Carnelley and W. C. Williams 209°±5°; and for the b.p. 327°, while A. Michaelis gave 324°. W. Herz gave 7·05 for the sp. gr.; 16·6 cals. per gram for the heat of fusion; and $2{\cdot}64\times10^{12}$ for the vibration frequency. The molten liquid is black; and the vapour has a colour not unlike that of iodine, but somewhat paler. The absorption spectrum was studied by D. Gernez, A. Wüllner, and W. Friederichs. When the reddish vapour of sulphur dichloride is heated it becomes paler and then assumes a yellow colour, and like tellurium tetrachloride it then shows no absorption spectrum. A. Voigt and W. Biltz found the electrical conductivity of the dichloride to be 0·042 mho at 206°; 0·0668 mho at 230°; 0·114 mho at 271°; and 0·151 at 305°. W. Biltz gave 0·042 for the temp. coeff. K. T. Compton gave 2·70 volt for the ionizing potential. A. Michaelis found that when the dichloride is heated in oxygen, it decomposes with incandescence forming the tetrachloride and dioxide. Water, acids, and alkali-lye were found by H. Rose to decompose the dichloride forming tellurous acid and tellurium. K. Lindner and L. Apolant said that water converts the dichloride into tellurium and oxydichloride. According to J. J. Berzelius, the same products are obtained when the dichloride is triturated with calcium oxide or sodium carbonate. M. Damiens found that an ethereal soln. of tellurium dichloride absorbs bromide forming which appears to be *tellurium chlorobromide;* and it absorbs iodine forming what may be *tellurium chloroiodide;* but neither substance could be isolated. J. J. Berzelius found that when a mixture of ammonium chloride and an alkali tellurite is heated *ammonium chlorotellurite,* $NH_4Cl.xTeCl_2$, is formed as a black sublimate, and when treated with a small proportion of water, the complex salt turns white owing to the separation of tellurous acid; this acid dissolves completely leaving tellurium behind; with a larger proportion of water, a mixture of tellurium

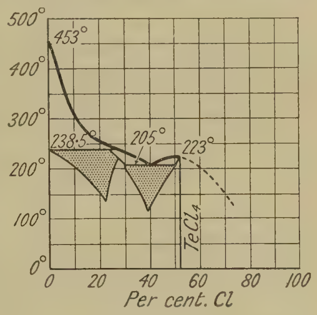


FIG. 43.—Freezing-point Curve of the System: Te–Cl.

and tellurous acid is precipitated. This may be separated by hydrochloric acid, and the water holds in soln. ammonium chlorotellurate and chloride. A. Gutbier and F. Flury—*vide* tellurium dioxide—said that the black sublimate is probably **tellurium diamminodichloride,** $TeCl_2.2NH_3$. K. Lindner and L. Apolant found that the repeated sublimation of the dichloride with a deficiency of ammonium chloride, yields **ammonium tetrachlorotellurite,** $(NH_4)_2TeCl_4$, as a greenish compact mass, which is not hygroscopic, and does not change in air. Tellurium trichloride may be fused with tellurium in all proportions; and when the mixture is heated in a retort, it first gives off tellurium dichloride, then metallic drops of a compound richer in tellurium—this is the only evidence for the existence of a *tellurium subchloride*—*cf.* Fig. 43. The residue left in the retort resembles tellurium, but is more easily powdered and reddens litmus. It is freed from the adherent chlorine by fusion in an atm. of hydrogen, or by boiling first with hydrochloric acid and afterwards with water.

As indicated in connection with tellurium dichloride, when an excess of chlorine acts on heated tellurium, **tellurium tetrachloride,** $TeCl_4$, mixed with some dichloride is formed. J. J. Berzelius, and A. Michaelis separated the mixture by fractional distillation. V. Lenher, and R. W. E. MacIvor also obtained it by passing the vapour of sulphur monochloride over heated tellurium. J. H. Simons also obtained it by distilling off the tetrachloride. Tellurium tetrachloride, at ordinary temp., is a snow-white crystalline mass. J. J. Berzelius found that it melts to an amber-yellow liquid, which becomes dark red near the b.p. A. Weller showed that it is an example of a colourless solid giving a coloured liquid, and vapour for the yellow vapour, said A. Wüllner, shows no absorption spectrum. J. H. Simons showed that the change in the colour of the vapour above 500° is due to the dissociation of the tetrachloride into dark red dichloride. J. H. Simons gave for the sp. gr. of the liquid:

	232°	277°	314°	341°	385°	424°	427°
Sp. gr. .	2·559	2·494	2·443	2·402	2·334	2·275	2·260

A. Michaelis found the vapour density (air unity) at 441° to be 9·03 to 9·22, and at 530°, 8·47 to 8·86. The calculated value for $TeCl_4$ is 9·33. J. H. Simons gave for the vapour density (H_2=2·016):

	420°	450°	480°	507°	522°	561°	601°
Vap. density .	290·3	283·1	277·7	273·2	269·1	260·2	250·5

It is concluded that the vapour consists of single molecules of $TeCl_4$ from the m.p. to about 500° where the dissociation $TeCl_4=TeCl_2+Cl_2$ begins. J. H. Simons gave for the surface tension, σ dynes per cm.:

	238°	260°	280°	316°	352·5°	370°	413·5
σ . . .	40·2	38·3	36·87	34·25	31·57	30·09	26·92

and the parachor ranges from 265·8 to 269·2. The vapour press., p mm.

	233°	260°	278·5°	313°	345°	360°	390°
p . . .	10·8	26·0	45·5	116·7	269·5	396·5	755·6

The results are taken to mean that the molecules of the vapour are associated only to a slight extent. T. Carnelley and W. C. Williams gave 224° for the m.p.; J. H. Simons, 225°; M. Damiens, 223°—Fig. 41; A. Michaelis, 214°. W. Biltz and H. Friedrich, 224°; and R. W. E. MacIvor, 214·5°. T. Carnelley and W. C. Williams gave 414° for the b.p.; J. H. Simons, 390°; and A. Michaelis, 380°—if the compound contains tellurium dioxide as impurity, the b.p. may appear higher. M. Wasilieff discussed the eutectic Te+$TeCl_4$. The heat of vaporization was found by J. H. Simons to be 18,400 cals. per mol. A. Voigt and W. Biltz gave for the electrical conductivity, 0·1145 mho at 236°; 0·161 mho at 271°; 0·203 at 316°; and W. Biltz gave for the temp. coeff. 0·11. J. H. Simons concluded that the molecule consists of a ten-electron shell surrounding a central atom, four parts of these being shared with chlorine atoms. S. Kyropoulos studied the dielectric constants of the crystals.

J. J. Berzelius, and V. Lenher found that the tetrachloride is stable in dry air; but in moist air, it deliquesces to a clear yellow liquid which gradually becomes turbid, and dries with the loss of hydrogen chloride to leave an oxychloride as residue. It dissolves completely in boiling water, and when the soln. cools, crystals of tellurium dioxide, accompanied by a little oxychloride, separate out. The aq. soln. behaves like a soln. of tellurium dioxide in hydrochloric acid. P. E. Browning and W. R. Flint said that in the hydrolysis of the tetrachloride, however large the proportion of water employed when hot, all the tellurous acid is precipitated, that which remains in soln. may be precipitated as dioxide by adding ammonia to the boiling soln., and then acetic acid; and they thought that the fraction remaining in soln. during the hydrolysis was a related dwi-tellurium—*vide supra*. They also showed that if tellurous oxide, freed from telluric oxide, is dissolved in hydrochloric acid which has been exposed to bright sunlight, and the soln. hydrolyzed with boiling water, the precipitate gives no chlorine when boiled with hydrochloric acid. R. Metzner said that tellurium tetrachloride dissolves in conc. hydrochloric acid, and the soln., sat. with hydrogen chloride at —30°, furnishes yellow needles of **tellurium hydropentachloride,** $TeCl_4.HCl$. This melts at —20°. It fumes in air giving off hydrogen chloride. W. Strecker and W. Ebert said that at 0°, white, hygroscopic **tellurium hexamminotetrachloride,** $TeCl_4.6NH_3$, is formed in ammonia gas; if the halide is at —80° the ammonia condensing on the tetrahalide produces a mixture which detonates when heated, presumably owing to the formation of nitrogen telluride (*q.v.*). V. Lenher found that tellurium tetrachloride is sparingly soluble in cold sulphur monochloride, but readily soluble in the hot liquid. C. Whitehead represented the reaction with tellurium hydride by $TeCl_4+2H_2Te=3Te+4HCl$. According to J. J. Berzelius, tellurium tetrachloride mixes with fused tellurium dichloride in all proportions—if the former predominates, the compound is yellow or dark red when liquid, and if the latter predominates, black. A. W. Ralston and J. A. Wilkinson found that at low temp. liquid hydrogen sulphide reduces the tetrachloride to the monochloride, and at ordinary temp., to tellurium. W. Prandtl and P. Borinsky found that sulphur trioxide reacts with tellurium tetrachloride forming the complex $TeCl_4.SO_3$. R. Metzner found that if ammonia be passed over tellurium tetrachloride at 200° to 250°, the colour blackens, owing to the separation of tellurium: $3TeCl_4+16NH_3=3Te+12NH_4Cl+2N_2$. At 0°, ammonia combines with the tetrachloride forming **tellurium triamminotetrachloride,** $TeCl_4.3NH_3$. This compound is not deliquescent; it gives off ammonia at ordinary temp.; it forms tellurous acid when treated with water; and gives off ammonia with alkali-lye. When heated it blackens, giving off ammonia, and at a higher temp. it forms tellurium dichloride, recognizable by the violet fumes. F. Wöhler and R. Espenschied said that even at ordinary temp. the tetrachloride absorbs ammonia forming **tellurium tetramminotetrachloride,** $TeCl_4.4NH_3$, as a voluminous, greenish-yellow mass which is stable in air. It is resolved by water into ammonium chloride and tellurous acid; and when heated is decomposed into tellurium, nitrogen, ammonium chloride, and hydrogen chloride. R. Metzner observed that molten tellurium tetrachloride at 220·5° dissolves phosphorus pentachloride, and furnishes a lemon-yellow crystalline mass of **tellurium phosphotridecachloride,** $2TeCl_4.PCl_5$. This becomes orange-yellow when hot. It forms a colourless liquid with a small proportion of water; but with a larger proportion of water, tellurous acid separates out. It sublimes with partial decomposition in air, but it is not so decomposed in the vapour of phosphorus pentachloride. A. M. Hageman observed that tellurium tetrachloride is soluble in benzene, toluene, methyl alcohol, ethyl alcohol, *n*-butyl alcohol, amyl alcohol, benzyl alcohol, xylene, chloroform, and ethyl acetate; sparingly soluble in light petroleum, benzaldehyde, acetone, *iso*propyl bromide, and carbon tetrachloride; and insoluble in carbon disulphide. According to J. J. Berzelius, the smallest trace of organic matter causes the tetrachloride to turn yellow on melting owing to the formation of some dichloride, which, at a higher temp., escapes as a violet vapour. According to V. Lenher, tellurium tetrachloride forms a complex $(C_2H_5)_2O.TeCl_4$, with ether; and a complex with methylamine. J. F. Norris and R. Mommers obtained a complex with dimethylamine; V. Lenher, complexes with ethylamine, trimethylamine, aniline, pyridine, and quinoline; and V. Lenher and W. Titus, complexes with quinine, cinchonine, morphine, theobromine, brucine, aconite, atropine, strychnine, and cocaine. H. D. K. Drew observed that cyclic condensation products are obtained with diphenyl ether and tellurium tetrachloride in chloroform soln.; G. T. Morgan and R. E. Kellett studied the interaction of the tetrachloride with anisole, etc.; G. T. Morgan and co-workers, monoketones, diketones, and triketones; G. T. Morgan and H. D. K. Drew, ethylene, acetylacetone, and acetic anhydride; G. T. Morgan and H. Burgess, dimethylaniline; and P. Falciola, thiocarbamide. Derivatives of *cyclo*telluripentane and *cyclo*telluropentane were prepared. D. K. Drew showed that $Te(CH_3)_2X_2$ readily passes into $Te(CH_3)_3X.TeCH_3X_3$, where X denotes a halogen atom. This is taken to mean that the compound has a tendency to get away from the unstable ten-electron shell by the association of two molecules to form an eight-electron shell to one tellurium atom, and a twelve-electron shell to the other. According to W. Biltz and K. Friedrich, metallic silver decomposes tellurium tetrachloride forming silver telluride and chloride; the excess of the tetrachloride has no action on silver telluride. Hence in its halogen compounds, tellurium behaves like a noble metal. A. Mazzucchelli and A. Vercillo found that copper furnishes a telluride, but not so with lead.

The higher halides of tellurium are more stable than those of sulphur and selenium. The tetrahalides of tellurium are most stable, whilst with selenium the lower halides are the most stable. The increase of basic properties observed in passing from selenium to tellurium is confirmed by the tellurium forming better-defined double halides. J. J. Berzelius prepared orange-yellow octahedral crystals of **ammonium hexachlorotellurite,** $(NH_4)_2.TeCl_6$, as a precipitate from a soln. of ammonium chloride and tellurium tetrachloride in hydrochloric acid. The salt was also prepared by W. Muthmann, and P. Köthner. C. F. Rammelsberg obtained yellow, cubic crystals of a salt which he represented by the formula $8NH_4Cl.3TeCl_4$, but this salt was probably impure hexachlorotellurite. P. Köthner said that the crystals are difficult to dry without decomposition. J. J. Berzelius said that the salt can be dissolved in a small proportion of water to form a colourless soln., but with a large proportion of water, or alcohol, the salt is decomposed. A. Gutbier prepared a number of complexes of the type $(R.NH_3)_2TeCl_6$ involving organic radicles. J. J. Berzelius, P. Köthner, and H. L. Wheeler obtained **potassium hexachlorotellurite,** K_2TeCl_6, in pale yellow, octahedral crystals from mixed hydrochloric acid soln. of potassium chloride and tellurium tetrachloride or a soln. of tellurium dioxide in hydrochloric acid. The crystals are stable in dry air, but they deliquesce in moist air; water decomposes them with the separation of tellurous acid and tellurium oxychloride. They are soluble in hydrochloric acid; and conc. hydrochloric acid or alcohol precipitates potassium chloride from this soln. C. F. Rammelsberg's formula, $8KCl.3TeCl_4$, is supposed to be based on the analysis of an impure salt. H. L. Wheeler, and P. Köthner likewise prepared **rubidium hexachlorotellurite,** Rb_2TeCl_6, in yellow octahedra, stable in air. H. L. Wheeler found that at 22°, 100 parts of hydrochloric acid of sp. gr. 1·05 dissolve 13·09 parts of the salt, and an acid of sp. gr. 1·2, 0·34 part. By a similar process, H. L. Wheeler prepared **cæsium hexachlorotellurite,** Cs_2TeCl_6, in yellow

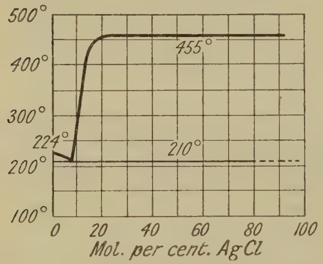


FIG. 44.—Freezing-point Curve of the Binary System: $TeCl_4$–AgCl.

octahedra; he found that at 22°, 100 parts of hydrochloric acid of sp. gr. 1·05 dissolve 0·78 part of the salt, and an acid of sp. gr. 1·2, 0·05 part. W. Biltz and H. Friedrich found that when tellurium tetrachloride is melted in sealed tubes with silver chloride, the liquid separates into two layers when over 20 molar per cent. AgCl is present. The lower liquid is almost all silver chloride and it freezes at 440°–455°; while the upper layer contains a eutectic mixture with the excess of silver chloride. The eutectic at 210° contains about 9 molar per cent. of AgCl—Fig. 44. No *silver tellurium chloride* is formed. R. Weber heated a mixture of aluminium trichloride and tellurium tetrachloride in a sealed tube, and drove off the excess of the former, by the application of a stronger heat, and there remained **aluminium decachlorotellurite,** $2AlCl_3.TeCl_4$. This compound is decomposed at an elevated temp.; it is hydrolyzed by water with the separation of tellurous acid; and it dissolves completely in dil. sulphuric acid.

J. J. Berzelius [3] said that bromine unites with tellurium at ordinary temp. with the development of heat; and he obtained **tellurium dibromide,** $TeBr_2$, by sublimation from a mixture of tellurium and its tetrabromide. The dibromide appears as a greenish-black crystalline mass, or in needle-like crystals. The powder is yellowish-olive-green. J. J. Berzelius said that the vapour is dark violet; and, according to D. Gernez, its absorption spectrum has lines in the red and yellow. Tellurium dibromide was found by T. Carnelley and W. C. Williams to melt at approximately 280°; B. Brauner said approximately 210°; and, added J. J. Berzelius, the cold mass has no marked lustre, or crystalline fracture. T. Carnelley and W. C. Williams gave 339° for the b.p. at 760 mm.; and B. Brauner gave 280° in vacuo, and added that sublimation in vacuo begins at about 200°. As in the case of tellurium dichloride, the observations of M. Damiens, Fig. 45, show that as the compound solidifies it dissociates into a solid soln. of tellurium in the tetrabromide. B. Brauner found that the dibromide is decomposed by water: $2TeBr_2=Te+TeBr_4$; and in moist air, this change rapidly occurs. A conc. soln. of tartaric acid dissolves a part of the dibromide forming a greenish-brown soln. from which water precipitates tellurium.

According to J. J. Berzelius, **tellurium tetrabromide,** $TeBr_4$, is prepared by introducing bromine into a glass tube, sealed at one end, and cooled by immersion in ice, adding powdered tellurium, not in excess, with frequent stirring; the excess of bromine is removed by heating the mixture on a water-bath. B. Brauner removed the excess of bromine by a current of carbon dioxide; unchanged tellurium was removed by heating the mixture which converted the tellurium into volatile dibromide; and oxybromide was removed by sublimation in vacuo at 300°. C. von Hauer prepared the tetrabromide by adding bromine to a mixture of tellurium and dil. hydrobromic acid, until the tellurium dissolved; the ruby-red liquid was then evaporated on a water-bath. F. A. Gooch and A. W. Peirce warmed tellurium dioxide with an aq. soln. of potassium bromide and phosphoric acid; on concentrating the soln., ruby-red crystals of tellurium tetrabromide are formed.

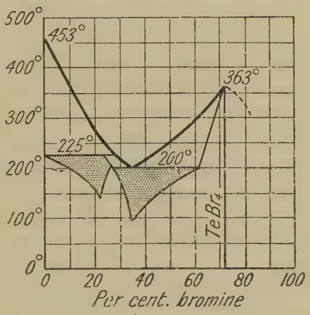


FIG. 45.—Freezing-point Curve of the System: Te–Br.

Tellurium tetrabromide, when obtained by sublimation, furnishes dark yellow prisms when slowly cooled, and fiery red or orange-red when rapidly cooled. B. Brauner found the sp. gr. to be 4·310 at 15°/4°. T. Carnelley and W. C. Williams gave 380° ± 6° for the m.p. J. J. Berzelius said that the molten liquid is dark red, and it forms a crystalline mass on solidification. M. Damiens gave 363° for the m.p.—Fig. 45. T. Carnelley and W. C. Williams found the b.p. to be 414° to 427°. J. J. Berzelius added that the vapour is yellow, and condenses to a yellow powder, needle-like crystals, etc. B. Brauner said that the tetrabromide cannot be melted or boiled under ordinary atm. press. without partial decomposition into tellurium dibromide. G. Beck studied the heat of soln. in water. S. Kyropoulos measured the dielectric constants of the crystals.

According to J. J. Berzelius, tellurium tetrabromide slowly absorbs moisture when exposed to air, and it dissolves without apparent decomposition in a small proportion of water; with a large proportion of water, the yellow liquid is resolved into tellurous and hydrobromic acids—the former appears as a precipitate. If the soln. in a small proportion of water is evaporated, it furnishes dark ruby-red, rhombic plates which, when dried, become yellow and earthy. B. Brauner found that the tetrabromide is soluble in an aq. soln. of tartaric acid (1 : 1), and the orange-yellow soln. can be diluted with water without separation owing to the formation of tellurium tartrate, tellurous acid, however, separates with a very dil. soln. of tartaric acid. According to R. Metzner, tellurium tetrabromide unites with hydrobromic acid with the evolution of heat; when the soln. is cooled to —15°, it furnishes orange-red, needle-like crystals of **tellurium hydropentabromide,** $TeBr_4.HBr.5H_2O$, which can be drained on a porous tile, and dried in dry air. The crystals melt at 20°, giving off hydrogen bromide. The crystals can be kept a long time at a low temp. in an atm. of hydrogen bromide; they are very deliquescent in air, and give off hydrogen bromide. W. Prandtl and P. Borinsky found that sulphur trioxide reacts with the tetrabromide forming $TeOH_2.SO_3$. According to W. Strecker and W. Ebert, the tetrabromide reacts with ammonia forming what is probably **tellurium hexamminotetrabromide,** $TeBr_4.6NH_3$, which then decomposes into nitrogen telluride (*q.v.*). V. Lenher observed that tellurium tetrabromide forms complex salts with methylamine, trimethylamine, ethylamine, aniline, pyridine, and quinoline; J. F. Norris and R. Mommers obtained a complex with dimethylamine; and V. Lenher and W. Titus, with quinine, cocaine, brucine, and morphine. A. Lowy and R. F. Dunbrook studied its action on primary, secondary, and tertiary amines; and E. H. Rusk, on phenols, and phenol ethers.

A number of **bromotellurites** has been prepared. W. Muthmann prepared **ammonium hexabromotellurite,** $(NH_4)_2TeBr_6$, from a soln. of ammonium bromide and tellurium dioxide in hydrobromic acid. The dark red, octahedral crystals are less soluble than the potassium salt. A. Gutbier and F. Flury prepared a number of complexes of the type $(R.NH_3)_2TeBr_6$ involving organic radicles. J. J. Berzelius prepared **potassium hexabromotellurite,** K_2TeBr_6, from a soln. of potassium chloride in one of tellurium bromide. C. von Hauer said that the product is contaminated with chloride, and he obtained the salt by adding bromine to a soln. of potassium bromide mixed with tellurium until that element had all dissolved. H. L. Wheeler used an excess of hydrobromic acid to prevent the precipitation of tellurous acid. The anhydrous salt separates from the boiling soln. in dark red octahedral crystals, which, according to W. Muthmann, are isomorphous with the corresponding bromoselenite. H. L. Wheeler found that the dihydrate, $K_2TeBr_6.2H_2O$, is formed by the evaporation of the aq. soln. at ordinary temp. C. von Hauer thought the salt is trihydrated, but H. L. Wheeler said that extra water in the latter case is present as inclusions. According to C. von Hauer, the dark red, opaque crystals resembling octahedra, belong to the rhombic system, for which W. J. Grailich and V. von Lang obtained the axial ratios $a : b : c = 0{\cdot}6857 : 1 : 0{\cdot}9415$; and H. Baker, $0{\cdot}6711 : 1 : 0{\cdot}9167$. The optical character is negative; there is no marked cleavage. The crystals effloresce superficially in dry air; and C. von Hauer found that they lose their water of crystallization at 120°, without melting; the dehydrated salt is orange-red. At a higher temp., tellurium tetrachloride is given off. J. J. Berzelius, C. von Hauer, and W. L. Wills observed that the salt dissolves in a small proportion of water, but if the soln. be diluted, tellurous acid is precipitated. H. L. Wheeler found that the salt can be recrystallized from dil. hydrobromic acid; and that at 22°, 100 parts of this acid of sp. gr. 1·08 dissolve 62·90 parts of salt, while with an acid of sp. gr. 1·49 there are 6·57 parts dissolved. J. J. Berzelius said that the salt is decomposed by alcohol. H. L. Wheeler prepared **rubidium**

hexabromotellurite, Rb_2TeBr_6, in an analogous manner. The red octahedral crystals are stable in air; they dissolve in a small proportion of hot water, and on cooling tellurous acid crystallizes out. At 22°, 100 parts of hydrobromic acid of sp. gr. 1·08 dissolve 3·08 parts of salt, and 0·25 part is dissolved by an acid of sp. gr. 1·49. Red octahedral crystals of **cæsium hexabromotellurite,** Cs_2TeBr_6, are obtained in a similar way. At 22°, 10 parts of hydrobromic acid of sp. gr. 1·08 dissolve 0·13 part of salt, and 0·02 part is dissolved by an acid of sp. gr. 1·49. P. Maier studied the crystallography of aliphatic bromotellurites.

Tellurium can be melted with iodine in all proportions, and, added J. J. Berzelius,[4] if the tellurium be in excess, the product has a metallic appearance, while if the iodine be in excess, the product is somewhat soluble in water. J. J. Berzelius found that when a gram-atom of tellurium is heated with more than a gram-atom of iodine, the excess of iodine passes off; and **tellurium diiodide,** TeI_2, sublimes in black, crystalline flakes having some metallic lustre, the fused mass readily sublimes, and the mass obtained by cooling the fused compound has a non-crystalline fracture. When digested with aq. hydrochloric acid, or aq. ammonia, it leaves a residue of tellurium; it is not attacked even by boiling water. A. Gutbier said that when tellurium and iodine are fused together in the requisite proportion to form tellurium diiodide, TeI_2, a black substance is produced which possesses a metallic lustre and melts easily. When very carefully heated, it can be sublimed, but its composition does not appear to be constant.

F. M. Jäger and J. B. Menke studied the f.p. curve of mixtures of the two elements. Tellurium tetraiodide was the only compound observed, and the molten substance is considerably dissociated. There is a eutectic on the tellurium side at 165° and 41 per cent. of tellurium, and this is near the composition required for tellurium di-iodide; on the iodine side, the eutectic at 108° is very near the iodine axis. Solid soln. are not formed to any appreciable extent, and there is no evidence of the formation of a *tellurium periodide*, or *tellurium hexaiodide*, which J. J. Berzelius said is formed when a piece of tellurium is dropped into molten iodine, after shaking the mixture, and decanting the liquid from the undissolved tellurium. The product was said to dissolve sparingly in water forming a dark brown liquid which is decolorized by ammonium sulphite, and which deposits tellurium on adding hydrochloric acid. M. Damiens f.p. curve of mixtures of iodine and tellurium is in general agreement with that of F. M. Jäger and J. B. Menke, and it is illustrated by Fig. 46. F. Olivari studied the effect of tellurium on the f.p. of iodine, and accordingly inferred that with about 94 per cent. of tellurium, the mol. wt. of tellurium is 159 to 171·2—the theoretical value for Te=127·6. E. Beckmann and R. Hanslian also found that cryoscopic and ebullioscopic measurements of soln. of tellurium in iodine indicate a large proportion of single atoms. R. Wright's measurements of the vap. press. of soln. of iodine and tellurium gave no indication of solid soln. or of the formation of any compound other than the tetraiodide.

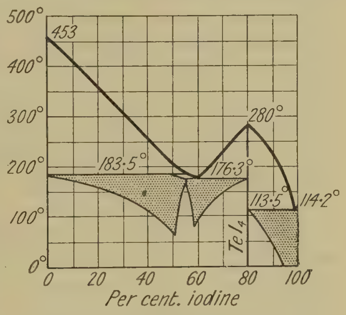


FIG. 46.—Freezing-point Curve of the System: Te–I.

J. J. Berzelius prepared **tellurium tetraiodide,** TeI_4, by digesting tellurium powder for a considerable time with iodine and water; and evaporating the clear liquid which gives off the excess of iodine and leaves a small proportion of the tetraiodide as residue. He also found that by digesting tellurium dioxide with hydriodic acid, in a closed vessel, it is slowly converted into the iron-grey tetraiodide. A small quantity of the tetraiodide dissolves in the excess of hydriodic acid imparting to it a dark brown colour, and may be separated from it in iron-grey prisms, by evaporation in vacuo over sulphuric acid and calcium oxide which takes up the excess of iodine and hydriodic acid. According to A. Gutbier and F. Flury, hydriodic acid acts on telluric acid in two ways. In dil. soln., reduction takes place slowly to tellurium dioxide, and after some time, a dark, granular mass of tellurium tetraiodide, TeI_4, separates. No indication was obtained of the formation of a di-iodide. In conc. soln., the reaction takes place quickly and tellurium tetraiodide is at once precipitated as a heavy iron-grey substance. Tellurium tetraiodide forms a dark-grey powder, or iron-grey prismatic crystals which melt when heated, and, according to A. Gutbier and F. Flury, it is at the same time decomposed. F. M. Jäger and J. B. Menke gave 259° for the m.p.; and M. Damiens, 280°. When boiled, the tetraiodide gives off at first iodine and the distillate becomes richer in tellurium until what was thought to be *tellurium subiodide* remained. The subiodide is probably tellurium contaminated with iodine.

J. J. Berzelius said that the tetraiodide is resolved by water into an oxyiodide which retains the form of the tetraiodide, and hydriodic acid holding a little tellurium tetraiodide in soln. Cold water has but a slight decomposing action and remains colourless, taking up only a small proportion of hydriodic acid; boiling water acquires a dark brown colour, and forms an oxyiodide. A. Gutbier and F. Flury said that the tetraiodide is decomposed by water: $TeI_4+2H_2O=4HI+TeO_2$, and a similar decomposition occurs with alcohol. The tetraiodide dissolves in aq. ammonia; it also dissolves in alkali-lye. According to J. J. Berzelius, when a sat. soln. of tellurium tetraiodide in conc. hydriodic acid is evaporated in vacuo over sulphuric acid, long, rectangular, four-sided prisms are obtained having a metallic lustre. R. Metzner obtained a similar product, **tellurium hydropentaiodide,** $TeI_4.HI.8$ or $9H_2O$, by passing hydrogen iodide into a soln. of tellurous acid in hydriodic acid. J. J. Berzelius said that in a sealed glass tube the crystals melt to a dark brown liquid which solidifies on cooling; and in an open vessel, at 50° to 60°, they do not melt, but give off brown fumes of hydrogen iodide decomposed by contact with air, and leave a residue of tellurium tetraiodide. R. Metzner said that when heated out of contact with air, the crystals melt at —55°, and solidify without chemical change on cooling; at a higher temp., they lose first water and then hydrogen iodide. The compound is decomposed by water yielding a precipitate of tellurium tetraiodide.

Tellurium tetraiodide unites with the iodides of the alkali metals forming **iodotellurites.** J. J. Berzelius prepared **ammonium hexaiodotellurite,** $(NH_4)_2TeI_6$, from a soln. of tellurium tetraiodide in hydriodic acid, neutralized with ammonia. The spontaneous evaporation of the liquid furnishes steel-grey octahedral crystals soluble in water and in absolute alcohol. J. J. Berzelius also reported that hydrated **sodium iodotellurite** crystallizes from an aq. soln. of the component salts, but this has not been confirmed. J. J. Berzelius prepared **potassium hexaiodotellurite,** $K_2TeI_6.2H_2O$, in a similar manner. The black prismatic crystals were found by H. L. Wheeler to belong to the monoclinic system, and to have the axial ratios $a:b:c=0{\cdot}7047:1:0{\cdot}5688$, and $\beta=120°\ 53°$. The crystals lose their water of crystallization, without decomposition, at 100° to 115°. They effloresce superficially in dry air. J. J. Berzelius added that they form a brown soln. with a small proportion of water, and are decomposed by a larger proportion of water. H. L. Wheeler similarly prepared **rubidium hexaiodotellurite,** Rb_2TeI_6, in microscopic octahedral crystals which are stable in air; and which are slowly decomposed by cold water, rapidly by hot water with the separation of tellurium dioxide and an oxyiodide. They dissolve in a small proportion of alcohol. H. L. Wheeler also prepared **cæsium hexaiodotellurite,** Cs_2TeI_6, as a black, amorphous precipitate which gradually loses iodine when exposed to air, and which melts at a little over the b.p. of sulphuric acid. It behaves like the rubidium salt towards water and alcohol.

REFERENCES.

[1] H. Moissan, *Ann. Chim. Phys.*, (6), **24**. 239, 1891; R. Metzner, *ib.*, (7), **15**. 203, 1898; *Sur quelques composés du sélénium et du tellure*, Paris, 1898; E. B. R. Prideaux, *Journ. Chem. Soc.*, **89**. 316, 1906; E. B. R. Prideaux and J. O'Neil Millott, *ib.*, **129**. 520, 1926; 2703, 1929; N. V. Sidgwick, *ib.*, **125**. 2672, 1924; A. J. Högbom, *Oefvers. Akad. Stockholm*, **38**. 1, 1882; *Bull. Soc. Chim.*, (2), **35**. 60, 1881; J. J. Berzelius, *Schweigger's Journ.*, **6**. 311, 1812; **34**. 78, 1823; *Pogg. Ann.*, **28**. 392, 1833; **32**. 1, 577, 1834; R. F. Weinland and J. Alfa, *Zeit. anorg. Chem.*, **21**. 43, 1899; H. L. Wells and J. M. Willis, *Amer. Journ. Science*, (4), **12**. 190, 1901.

[2] H. Rose, *Pogg. Ann.*, **21**. 443, 1831; R. Weber, *ib.*, **104**. 428, 1858; V. Lenher, *Journ. Amer. Chem. Soc.*, **22**. 136, 1900; **24**. 188, 1902; V. Lenher and W. Titus, *ib.*, **25**. 730, 1903; A. W. Ralston and J. A. Wilkinson, *ib.*, **50**. 258, 1928; A. Michaelis, *Ber.*, **20**. 2488, 1887; A. Wüllner, *ib.*, **20**. 1190, 1887; W. Muthmann, *ib.*, **26**. 1008, 1893; W. Strecker and W. Ebert, *ib.*, **58**. B, 2527, 1925; J. J. Berzelius, *Schweigger's Journ.*, **6**. 311, 1812; **34**. 78, 1823; *Pogg. Ann.*, **28**. 392, 1833; **32**. 1, 577, 1834; T. Carnelley and W. C. Williams, *Journ. Chem. Soc.*, **35**. 563, 1879; **37**. 125, 1880; J. F. Norris and R. Mommers, *Amer. Chem. Journ.*, **23**. 486, 1900; **25**. 730, 1903; D. Gernez, *Compt. Rend.*, **74**. 1190, 1872; W. Friederichs, *Ueber Absorptionsspectra von Dämpfen*, Bonn, 1905; *Zeit. wiss. Photochem.*, **3**. 154, 1905; R. W. E. MacIvor, *Chem. News*, **86**. 308, 1902; R. Metzner, *Ann. Chim. Phys.*, (7), **15**. 203, 1898; *Sur quelques composés du sélénium et du tellure*, Paris, 1898; H. L. Wheeler, *Amer. Journ. Science*, (3), **45**. 267, 1893; *Zeit. anorg. Chem.*, **3**. 428, 1893; W. Herz, *ib.*, **170**. 237, 1928; A. Gutbier and F. Flury, *ib.*, **37**. 152, 1903; **86**. 169, 1914; *Journ. prakt. Chem.*, (2), **86**. 150, 1912; A. M. Hageman, *Journ. Amer. Chem. Soc.*, **41**. 329, 1919; C. F. Rammelsberg, *Sitzber. Akad. Berlin*, 386, 1875; F. Wöhler and R. Espenschied, *Liebig's Ann.*, **113**. 105, 1860; R. Espenschied, *Ueber das Stickstoffselen*, Göttingen, 1859; P. Köthner, *Liebig's Ann.*, **319**. 1, 1901; *Das reine Tellur und sein Atomgewicht*, Halle, 1901; M. Damiens, *Ann. Chim.*, (9), **19**. 44, 1923; *Recherches sur le tellure et ses dérivés halogènés*, Paris, 1922; C. Whitehead, *Journ. Amer. Chem. Soc.*, **17**. 849, 1895; A. G. V. Harcourt and H. G. Baker, *Journ. Chem. Soc.*, **99**. 1311, 1911; H. D. K. Drew, *ib.*, **129**. 223, 1926; G. T. Morgan and R. E. Kellett, *ib.*, **129**. 1080, 1926; G. T. Morgan and H. D. K. Drew, *ib.*, **121**. 922, 1922; **127**. 531, 2307, 1925; G. T. Morgan, H. D. K. Drew, and T. V. Barker, *ib.*, **117**. 1457, 1920; **121**. 2412, 1922; G. T. Morgan and O. C. Elvine, *ib.*, **127**. 2625, 1925; G. T. Morgan and C. R. Porter, *ib.*, **125**. 1269, 1924; G. T. Morgan and H. Burgess, *ib.*, 321, 1928; D. K. Drew, *ib.*, 560, 1929; P. E. Browning and W. R. Flint, *Amer. Journ. Science*, (4), **28**. 112, 347, 1909; *Zeit. anorg. Chem.*, **64**. 104, 112, 1909; P. E. Browning and G. O. Oberhelman, *Proc. Internat. Congress Appl. Chem.*, **8**. ii, 59, 1912; W. Biltz and H. Friedrich, *Zeit. anorg, Chem.*, **136**. 416, 1924; W. Biltz, *ib.*, **133**. 307, 1924; A. Voigt and W. Biltz, *ib.*, **133**. 277, 1924; K. Lindner and L. Apolant, *ib.*, **136**. 381, 1924; W. Prandtl and P. Borinsky, *ib.*, **62**. 237, 1909; P. Borinsky, *Ueber die Einwirkung von Schwefeltrioxyd und dessen Chlorosubstitutionsprodukten auf Schwefel, Selen und Tellur*, München, 1909; P. Falciola, *Annali Chim. Appl.*, **17**. 359, 1927; K. T. Compton, *Phys. Rev.*, (2), **8**. 412, 1916; A. Mazzucchelli and A. Vercillo, *Atti Accad. Lincei*, (6), **1**. 233, 1925; A. M. Wasilieff, *Journ. Russ. Phys. Chem. Soc.*, **42**. 428, 1910; A. Weller, *Ber.*, **60**. B, 649, 1927; J. H. Simons, *Journ. Amer. Chem. Soc.*, **52**. 3483, 3488, 1930; S. Kyropoulos, *Zeit. Physik*, **63**. 849, 1930.

[3] J. J. Berzelius, *Schweigger's Journ.*, **6**. 311, 1812; **34**. 78, 1823; *Pogg. Ann.*, **28**. 392, 1833; **32**. 1, 577, 1834; C. von Hauer, *Journ. prakt. Chem.*, (1), **73**. 98, 1858; *Sitzber. Akad. Wien*, **25**. 142, 1857; D. Gernez, *Compt. Rend.*, **74**. 1190; 1872; W. L. Wills, *Liebig's Ann.*, **202**. 246, 1880; *Journ. Chem. Soc.*, **35**. 704, 1879; T. Carnelley and W. C. Williams, *ib.*, **35**. 563, 1879; **37**. 125, 1880; H. Baker, *ib.*, **35**. 712, 1879; B. Brauner, *ib.*, **35**. 381, 1889; **67**. 549, 1895; *Monatsh.*, **10**. 411, 1889; *Sitzber. Akad. Wien*, **98**. 456, 1889; W. J. Crailich and V. von Lang, *ib.*, **27**. 18, 1857; R. Metzner, *Compt. Rend.*, **126**. 1716, 1898; *Ann. Chim. Phys.*, (7), **15**. 203, 1898; *Sur quelques composés du sélénium et du tellure*, Paris, 1898; E. H. Rusk, *Ber.*, **30**. 1828, 1897; W. Damiens, *Recherches sur le tellure et des dérivés halogènés*, Paris, 1922; *Compt. Rend.*, **173**. 300, 583, 1921; *Ann. Chim.*, (9), **19**. 44, 1923; H. L. Wheeler, *Amer. Journ. Science*, (3), **45**. 267, 1883; *Zeit. anorg. Chem.*, **3**. 428, 1893; F. A. Gooch and A. W. Peirce, *ib.*, **12**. 118, 1896; *Amer. Journ. Science*, (4), **1**. 181, 1896; W. Prandtl and P. Borinsky, *Zeit. anorg. Chem.*, **62**. 237, 1909; P. Borinsky, *Ueber die Einwirkung von Schwefeltrioxyd und dessen Chlorosubstitutionsprodukten auf Schwefel, Selen und Tellur*, München, 1909; J. F. Norris and R. Mommers, *Amer. Chem. Journ.*, **23**. 486, 1900; V. Lenher, *Journ. Amer. Chem. Soc.*, **22**. 136, 1900; V. Lenher and W. Titus, *ib.*, **25**. 730, 1903; A. Lowy and R. F. Dunbrook, *ib.*, **44**. 614, 1922; W. Muthmann, *Ber.*, **26**. 1008, 1893; W. Strecker and W. Ebert, *ib.*, **58**. B, 2527, 1925; A. Gutbier and F. Flury, *Zeit. anorg. Chem.*, **86**. 169, 1914; *Journ. prakt. Chem.*, (2), **86**. 150, 1912; P. Maier, *Zeit. Kryst.*, **56**. 241, 1921; G. Beck, *Zeit. anorg. Chem.*, **174**. 31, 1928; S. Kyropoulos, *Zeit. Physik*, **63**. 849, 1930.

[4] J. J. Berzelius, *Schweigger's Journ.*, **6**. 311, 1812; **34**. 78, 1823; *Pogg. Ann.*, **28**. 392, 1833; **32**. 1, 577, 1834; R. Metzner, *Compt. Rend.*, **126**. 1716, 1898; *Ann. Chim. Phys.*, (7), **15**. 203, 1898; *Sur quelques composés du sélénium et du tellure*, Paris, 1898; H. L. Wheeler, *Amer. Journ. Science*, (3), **45**. 267, 1883; *Zeit. anorg. Chem.*, **3**. 428, 1893; A. Gutbier and F. Flury, *Zeit. anorg. Chem.*, **32**. 108, 1902; A. Gutbier, *Studien über das Tellur*, Leipzig, 1901; *Zeit. anorg. Chem.*, **32**. 292, 1902; M. Damiens, *Compt. Rend.*, **171**. 1140, 1920; **172**. 447, 1105, 1921; *Recherches sur le tellure et ses dérivés halogènés*, Paris, 1922; *Ann. Chim. Phys.*, (9), **19**. 44, 1923;

W. Hampe, *Chem. Ztg.*, **12**. 122, 1888 ; F. M. Jäger and J. B. Menke, *Proc. Acad. Amsterdam*, **14**. 724, 1912 ; *Zeit. anorg. Chem.*, **75**. 241, 1912 ; **77**. 320, 1912 ; J. B. Menke, *ib.*, **77**. 282, 1912 ; E. Beckmann and R. Hanslian, *ib.*, **80**. 221, 1913 ; R. Hanslian, *Molekulargewichtsbestimmungen in gefrierenden und Biedendem Iod*, Weida i. Th., 1910 ; F. Olivari, *Atti Accad. Lincei*, (5), **18**. ii, 384, 1909 ; R. Wright, *Journ. Chem. Soc.*, **107**. 1527, 1915.

§ 13. The Oxyhalides of Tellurium

According to A. Ditte[1] tellurium dioxide absorbs hydrogen fluoride with the development of heat. A. Metzner observed that tellurium dioxide dissolves in 43 to 55 per cent. hydrofluoric acid and on cooling to —20°, long, transparent crystals of **tellurium hexoxyoctofluoride,** $2TeF_4.3TeO_2.6H_2O$, separate. These crystals decompose when heated in hydrogen forming tellurium tetrafluoride, and fluoriferous tellurium dioxide ; they are decomposed by water : $2TeF_4.3TeO_2.6H_2O = 5TeO_2 + 8HF + 2H_2O$. E. B. R. Prideaux and J. O'Neil Millott did not obtain this product in their study of the action of hydrofluoric acid on tellurium dioxide. They measured the solubilities of tellurium dioxide in aq. hydrofluoric acid at 10°, and found that with the following concentrations in grms. per 100 grms. of HF and of TeO_2,

[HF] .	0·221	1·22	7·83	10·0	13·0	15·8	17·5	22·6
[TeO_2]	0·120	1·26	16·8	24·0	44·5	46·2	50·2	43·0
[HF] .	20·5	15·2	16·5	14·8	18·2	24·0	26·4	28·5
[TeO_2]	59·0	54·0	55·7	57·0	50·5	42·6	45·7	58·0

The results with the concentrations expressed in mols of the constituent per 100 mols of soln. are plotted in Fig. 47. The addition of tellurous acid, $H_2TeO_3 \rightleftharpoons H^{\cdot} + HTeO'_3$, to hydrofluoric acid represses the ionization of the hydrofluoric acid, $H_2F_2 \rightleftharpoons H^{\cdot} + HF_2'$, and removes it as a complex ion of the complex fluoride : $2H^{\cdot} + HTeO_3' + HF_2' \rightleftharpoons 2H^{\cdot} + TeF_2O_2'' + H_2O$; and the acid then crystallizes from the aq. soln. as the dihydrate : $2H_2[TeO_2F_2] \rightarrow 2(TeOF_2.H_2O) = TeF_4.TeO_2.2H_2O$. R. Metzner found that when the mother-liquor obtained in the preparation of this salt just described is more strongly cooled, with frequent stirring, needle-like crystals of **tellurium oxydifluoride,** $TeF_2.TeO_2.2HF$, *i.e.* $2TeO_2.4HF$, or **telluryl difluoride,** $TeOF_2.H_2O$, are formed. E. B. R. Prideaux and J. O'Neil Millott preferred the formula $TeF_4.TeO_2.H_2O$, and were unable to decide whether to write it $2TeOF_2.H_2O$, or $TeOF_2TeO_2.2HF$. A. J. Högbom, and E. B. R. Prideaux and J. O'Neil Millott obtained crystals of the oxyfluoride by evaporating an aq. soln. in vacuo over conc. sulphuric acid. R. Metzner found that when the salt is heated, it yields tellurium dioxide and hydrogen fluoride ; and that it is decomposed by water.

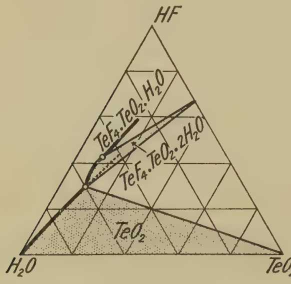


FIG. 47.—The Ternary System : $HF–TeO_2–H_2O$ at 10°.

R. F. Weinland and J. Alfa said that conc. hydrofluoric acid reacts with potassium tellurate forming **potassium difluotellurate,** $K_2TeO_3F_2.3H_2O$, in which an atom of oxygen is replaced by two atoms of fluorine ; but it may also be represented $K_2TeO_4.2HF.2H_2O$. It is obtained by evaporating a soln. of a mol of telluric acid and 2 mols of potassium hydroxide to dryness on the water-bath and dissolving the residue in a slight excess of hydrofluoric acid ; it crystallizes in microscopic, octahedral, monoclinic crystals, is fairly stable in dry air, but when heated evolves water and a small quantity of hydrogen fluoride, or at a higher temp. oxygen, and leaves a residue of tellurium dioxide and potassium fluoride. It is difficult to dissolve in water, yielding a faintly acid soln. and cannot be recrystallized from hydrofluoric acid. The corresponding **rubidium difluotellurate,** $Rb_2TeO_3F_2.3H_2O$, similarly prepared, furnishes colourless crystals rather more soluble than the potassium salt. Neither *ammonium difluotellurate,* nor *sodium difluotellurate* could be prepared.

J. J. Berzelius obtained a number of **tellurium oxychlorides** of undetermined composition—*e.g.* by the action of cold water on tellurium tetrachloride; from a soln. of the tetrachloride in boiling water; by exposing the tetrachloride to moist air; by evaporating a soln. of the tetrachloride on the water-bath; by dissolving the tetrachloride in hydrochloric acid, by evaporating a hydrochloric acid soln. of telluric acid; and from a soln. of tellurium in aqua regia. A. Michaelis obtained oxychlorides from a soln. of tellurium dioxide in molten tellurium tetrachloride. According to A. Ditte, tellurium dioxide readily absorbs hydrogen chloride with the development of heat and the formation of a brown mass. If the temp. be below —10°, the product has the composition *tellurium dioxytrihydrotrichloride,* $TeO_2.3HCl$; by slightly raising the temp. *tellurium dioxydihydrodichloride,* $TeO_2.2HCl$, is formed, and this can be heated to 90° without decomposition. T. W. Parker and P. L. Robinson observed no evidence of the formation of a complex $TeO_2.n.HCl$ in the range of temp. 0° to 150°. At 0°, hydrogen chloride is absorbed to form a heterogeneous product which loses water continuously in a stream of gas as the temp. is raised. At about 110°, it melts to a brown liquid forming **tellurium oxydichloride,** or **telluryl dichloride,** $TeOCl_2.H_2O$, and the reaction is completed at 300°. If heated to a still higher temp., the oxydichloride is decomposed into tellurium tetrachloride and dioxide: $2TeOCl_2=TeO_2+TeCl_4$. V. Lenher also prepared the complex $TeO_2.2HCl$, but showed that it is not converted into the oxydichloride by heat but rather into a mixture of the tetrachloride and dioxide without the intermediate formation of an oxydichloride. If the tetrachloride and dioxide are heated together, no combination occurs, and on cooling the original compounds can be removed unchanged. K. Lindner and L. Apolant said that the oxydichloride is formed, with the separation of tellurium, by the action of water on tellurium dichloride.

J. J. Berzelius obtained tellurium **oxybromides** of undetermined composition—*e.g.* by exposing **tellurium** tetrabromide to moist air; and by the action of water on the tetrabromide. A. Ditte found that tellurium dioxide at ordinary temp. absorbs hydrogen bromide with the development of heat forming a dark brown, crystalline mass which at —14° absorbs more of the gas to form a black, crystalline mass of *tellurium dioxytrihydrotribromide,* $TeO_2.3HBr$; if the temp. be raised not over 40°, this passes into tellurium dioxydihydrodibromide, $TeO_2.2HBr$, which begins to lose water when heated to 70°, and forms **tellurium oxydibromide** or **telluryl bromide,** $TeOBr_2$, when heated up to 300°. At a higher temp., the pale yellow mass melts and decomposes $2TeOBr_2=TeO_2+TeBr_4$.

J. J. Berzelius obtained **tellurium oxyiodides** of undetermined composition—by boiling tellurium tetraiodide with successive quantities of water; by evaporating a sat. soln. of the tetraiodide in conc. hydriodic acid; and from a soln. of telluric acid in hydriodic acid. A. Ditte found that tellurium dioxide absorbs hydrogen iodide at —15°, but at ordinary temp., the dioxide is decomposed. The absorption at —15° is very slow because the dioxide agglomerates together. He was unable to fix as much as one eq. of the hydrogen iodide with the tellurium dioxide; and as the temp. rises, the product decomposes forming tellurium iodide.

REFERENCES.

[1] J. J. Berzelius, *Schweigger's Journ.*, **6**. 311, 1812; **34**. 78, 1823; *Pogg. Ann.*, **28**. 392, 1833; **32**. 1, 577, 1834; A. J. Högbom, *Bull. Soc. Chim.*, (2), **35**. 60, 1881; *Oefvers. Akad. Stockholm*, **38**. 1, 1882; R. Metzner, *Compt. Rend.*, **126**. 1716, 1898; *Ann. Chim. Phys.*, (7), **15**. 203, 1898; *Sur quelques composés du sélénium et du tellure*, Paris, 1898; *Compt. Rend.*, **125**. 23, 1897; A. Ditte, *ib.*, **83**. 336, 446, 1876; A. Michaelis, *Ber.*, **20**. 2488, 1887; V. Lenher, *Journ. Amer. Chem. Soc.*, **31**. 243, 1909; E. B. R. Prideaux and J. O'Neil Millott, *Journ. Chem. Soc.*, **129**. 167, 520, 1926; 2703, 1929; T. W. Parker and P. L. Robinson, *ib.*, 2853, 1928; R. F. Weinland and J. Alfa, *Zeit. anorg. Chem.*, **21**. 43, 1899; K. Lindner and L. Apolant, *ib.*, **136**. 381, 1924.

§ 14. Tellurium Sulphides

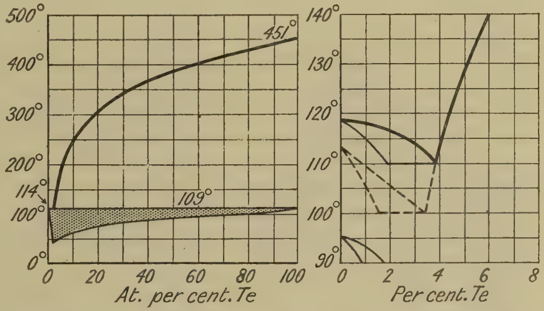
According to J. J. Berzelius,[1] H. Rose, F. Becker, B. Brauner, L. Staudenmaier, A. M. Hageman, and A. Gutbier and F. Flury, the precipitate produced by hydrogen sulphide in a hydrochloric acid soln. of tellurium dioxide in hydrochloric acid, or an acidified soln. of an alkali tellurite, is unstable **tellurium disulphide,** TeS_2. M. Chikasige also said that the alleged disulphide is really a mixture. When first formed, the precipitate is red, but it very quickly turns brown, brownish-black, and finally black, owing to the decomposition of the sulphide into its elements; and if the dried precipitate be extracted with carbon disulphide, all but 1 to 4 per cent. of the sulphur can be removed. B. Brauner thought that the sulphur so retained was evidence that a more stable sulphide is associated with the ordinary disulphide, but F. Becker, A. H. Hageman, and L. Staudenmaier said that the sulphur is very intimately mixed with the tellurium and inaccessible to the solvents; and is not present as tellurium sulphide decomposable by hydrochloric acid or as a variety of sulphur insoluble in carbon disulphide. A. M. Hageman found that at temp. below —20°, tellurium disulphide is stable, but above —20° dissociation sets in; and at —20° dissociation is slow, and becomes more rapid as the temp. is raised. The progress of the dissociation can be measured by the proportion of sulphur extracted by carbon disulphide, but the reaction is never complete—at least 0·95 per cent. of sulphur remains. The production of tellurium disulphide is independent of the conc. of the acid, and of the medium in which the reaction is effected—*e.g.* ether, and other organic solvents can be used instead of water as solvent. The dissociation and stability of the disulphide is solely a question of temp. A. Gutbier and F. Flury suggested that the precipitate at the moment of the formation is *sulphotellurous acid*, H_2TeS_3, or the complex $H_2TeS_3.2H_2S$. A. Gutbier found that a pseudo-solution, or a soln. of **colloidal tellurium disulphide** is formed as a transparent liquid with a blue fluorescence. After dialysis, the sol. keeps well; and by freezing, a solid hydrosol is produced. R. Astfalk also investigated the colloidal disulphide.

The bluish-black product, alleged to be the disulphide, TeS_2, according to J. J. Berzelius, acquires a metallic lustre when burnished. It softens when heated without melting completely; swells up; and solidifies on cooling to form a blistered, grey mass. When heated in a retort, sulphur distils off leaving a residue of tellurium; a mixture of the product with a metal sulphide leaves a residue of the metal telluride. The alleged tellurium disulphide forms a yellow soln. with boiling alkali-lye; and when freshly precipitated, dissolves sparingly in conc. aq. ammonia. R. W. E. MacIvor said that the fresh precipitate dissolves in a soln. of ammonium sulphide, but owing to the decomposition of the disulphide, some tellurium remains undissolved.

W. O. Snelling said that at the moment of precipitation of tellurium sulphide by hydrogen sulphide in an aq. soln. of tellurous acid, only half the sulphur is soluble in carbon disulphide, and that the insoluble residue consists of **tellurium monosulphide,** TeS, supposed to be formed in accord with: $2H_2S+H_2TeO_3=TeS+S+3H_2O$. This compound is said to be very unstable and to decompose completely in about 4 hrs. at 0°, and much more rapidly at higher temp. A. M. Hageman said that the alleged monosulphide has no existence.

According to J. J. Berzelius, if a dil. aq. soln. of telluric acid be sat. with hydrogen sulphide, and set aside in a closed vessel in a warm place, it turns brown without losing its colour; afterwards the colour disappears, and **tellurium trisulphide,** TeS_3, is deposited as a greyish-black, shining film which is easily rubbed off in flakes. According to F. Becker, B. Brauner, and A. Gutbier and F. Flury, the precipitate has the composition Te : 3S, and during its formation some telluric acid is reduced to tellurous acid. A. Gutbier and F. Flury added that there is no sign of the formation of a *sulphoxytelluric acid*. B. Brauner, and F. Becker found that the alleged tellurium trisulphide gives up nearly all its sulphur to carbon disulphide—F. Becker found about 6·15 per cent. escaped extraction. B. Brauner said that the sulphur is completely volatilized when the trisulphide is heated in a current of an indifferent gas. He observed that telluric acid resembles arsenic acid, but it surpasses it in so far as it is acted on by that reagent with far greater difficulty. It is also far more difficult to reduce by sulphurous acid. It differs from arsenic acid in so far as no *sulphoxytelluric acid* is formed in the cold. It resembles antimonic acid in the arrangement of atoms corresponding with the formation of a sulphoxytelluric acid being very unstable, but it differs from it in that if the acid in question is formed at a high temp. it is immediately destroyed. Tellurium differs, however, most essentially both from arsenic and from antimony, in the fact that tellurous acid and telluric acid when precipitated with hydrogen sulphide, give, as a final product of the action, precipitates consisting almost entirely of free tellurium and of free sulphur in the at. proportions $Te+S_2$ or $Te+S_3$. It is therefore impossible to investigate the question whether telluric acid, when treated with hydrogen sulphide under certain conditions, gives the disulphide, and under other conditions the trisulphide, in the same way as could be done with arsenic and antimony, for their sulphides are relatively stable. A. Gutbier found that when a small proportion of hydrogen sulphide is passed into a dil. soln. of telluric acid, a soln. of colloidal tellurium trisulphide is formed. It is steel-blue to violet by transmitted light.

J. J. Berzelius stated that tellurium and sulphur may be melted together in all proportions—with an excess of sulphur, the mixture is yellowish-red; as the proportion of tellurium is increased, the mixture appears red by transmitted light, and black by reflected light; and with a still higher proportion of tellurium, an opaque, lead-grey mixture is produced. G. Pellini showed that the f.p. curves furnish no indication of the formation of a compound, but a series of mixed crystals may be obtained both by fusion and by soln. Some of these crystals are isomorphous with rhombic sulphur, Figs. 1 and 2, for instance, those containing 0·557 per cent. of tellurium, have the axial ratios $a:b:c=0{\cdot}8136:1:1{\cdot}86929$, while artificial sulphur crystals have the ratios 0·8108 : 1 : 1·9005. A solid amorphous soln. of tellurium and sulphur was obtained which is insoluble in carbon trisulphide. The red sulphur of Japan is said to be an isomorphous mixture of sulphur, selenium, and tellurium. The f.p. curves of mixtures of sulphur and selenium, and of selenium and tellurium have been discussed in connection with selenium sulphide and tellurium selenide. G. Pellini's observations on sulphur and tellurium are illustrated in Figs. 48 and 49. Fig. 49 shows an enlargement of the f.p. curves in the vicinity of the eutectic. M. Chikashige found that two series of solid soln. are formed of limited concentration and the eutectic given by M. Chikashige is at 109° and 7 per cent. of tellurium. F. M. Jäger gave 106° for the eutectic. According to M. Chikashige, the transformation temp. of sulphur at 120° and 94·5° are lowered by tellurium. Whilst β-sulphur retains 2 per cent. of tellurium in solid soln., α-sulphur retains only 0·5 per cent., but the separation of the excess occurs only under the influence of light. Molten β-sulphur dissolves 10 per cent. of tellurium, and molten γ-sulphur, 20 per cent. Solid soln. with less than 0·5 per cent. of tellurium—including Japanese red sulphur—are not sensitive to light. The supersaturated crystals containing from 0·5 to 2·0 per cent. of tellurium change from red to yellow or brown when exposed to light; the most active rays have a wave-length $\lambda=4500$. The decomposed portions are more readily dissolved by



Figs. 48 and 49.—Fusion Curve of Mixtures of Sulphur and Tellurium.

carbon dioxide than the original crystals. L. Losana confirmed G. Pellini's value of 1·9 per cent. for the limit of complete miscibility, and he found the minimum on the liquid curve was at 6 per cent. tellurium and the maximum eutectic arrest corresponds with this. When over 97·6 per cent. of tellurium is present, there is no trace of an arrest showing that there is a zone of solid soln. with 98 to 100 per cent. tellurium. L. Losana found that the ternary system exhibits formation of neither compounds nor ternary eutectics, but contains two zones of complete miscibility in which there exist mixed crystals of selenium and tellurium in sulphur and mixed crystals of sulphur and tellurium in selenium. The formation of mixed sulphur-tellurium crystals is favoured by the presence of selenium, which causes solid soln. with high proportions of tellurium to be formed; many of such solid soln. exhibit, however, the phenomenon of more or less rapid unmixing. The first transformation point of sulphur is depressed considerably by selenium and tellurium separately and to a still greater extent by the two elements together. L. Losana's observations are summarized in Figs. 50, 51, and 52. According to L. Amaduzzi and M. Padoa, mixtures of sulphur and selenium are devoid of photo-electric properties.

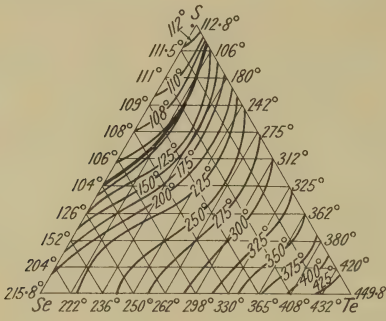


FIG. 50.—Liquidus Curves in the Ternary System: Se–S–Te.

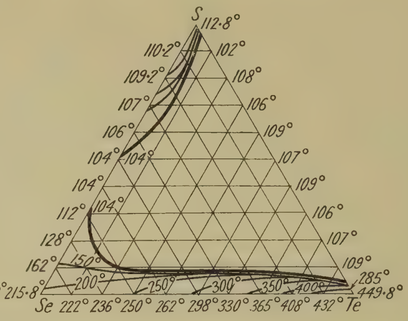


FIG. 51.—Solidus Curves in the Ternary System: Se–S–Te.

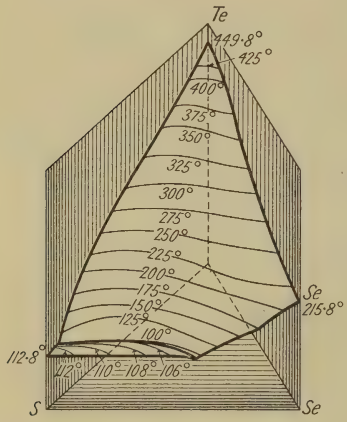


FIG. 52.—Projection of the Liquidus Curves in the Ternary System: Se–S–Te.

A. Stock and P. Praetorius observed that when an arc is maintained under carbon disulphide between a graphite cathode and an anode of tellurium and graphite (10 : 1), the anode is disintegrated, and a reddish-brown soln. is produced in which black particles of tellurium and graphite are suspended. The soln. contains non-volatile decomposition products of carbon disulphide, and carbon subsulphide, (C_3S_2), and **carbon sulphotelluride,** CSTe, which are volatile in the vapour of carbon disulphide. Part of the carbon subsulphide can be removed by fractional distillation; and the remainder by transforming it into a non-volatile thiomalono-naphthylamide by treatment with β-naphthylamine. The dil. soln. was concentrated on a water-bath, and subsequently cooled below —30° when the sulphotelluride was obtained in yellowish-red crystals with a penetrating odour of garlic. If it be smelled for a short time, the breath retains a strong odour of garlic for a considerable time. Cryoscopic and ebulliscopic measurements in benzene or carbon disulphide soln. are in agreement with the formula CSTe. The sp. gr. of the crystals at —50° is 2·9, and the vap. press. at 10° is about 2 mm. The crystals melt at —54° to a brilliant red liquid with a high refractive power. Carbon sulphotelluride, either solid or in soln., becomes blood-red, then black, and decomposes rapidly on attaining room temp. Some decomposition occurs even at —50°. When the soln. in carbon disulphide is treated with bromine, it gives a precipitate of tellurium tetrabromide; and mercury extracts all the compound from its soln. Carbon sulphotelluride is the compound which was previously thought to be carbon ditelluride (*q.v.*).

Salts of the hypothetical *sulphotellurous acid*, H_6TeS_5, have been prepared, as **sulphotellurites.** J. J. Berzelius said that the sulphotellurites of the alkali metals and magnesium are produced by saturating the soln. of the corresponding tellurite with hydrogen sulphide: $3R_2TeO_3+9H_2S=R_6TeS_5+2Te+4S+9H_2O$; they are also produced by the action of a boiling soln. of the alkali hydrosulphides on tellurium dioxide; and by dissolving tellurium disulphide in alkali-lye: $5TeS_2+18KOH=3K_2TeO_3+2K_6TeS_5+9H_2O$. The salts of the alkaline earths and of the heavy metals can be produced by double decomposition of a salt of these elements with the alkali sulphotellurite. The alkali sulphotellurites are brownish-yellow when anhydrous, and pale yellow when hydrated. They can be heated to redness without decomposition if protected from air. The sulphotellurites of the heavy metals are decomposed when heated out of contact with air, forming a metal telluride and basic sulphide. The sulphotellurites are fairly stable in air; freely soluble in water. The aq. soln. decomposes rapidly in air forming a soluble thiosulphate and precipitating a mixture of sulphur and tellurium. The salts dissolve in alcohol with partial decomposition. Acids precipitate tellurium disulphide. J. J. Berzelius reported that **ammonium sulphotellurite,** $3(NH_4)_2S.TeS_2$, or $(NH_4)_6TeS_5$, separates when a soln. of ammonium tellurite is sat. with hydrogen sulphide, and evaporated in vacuo over potassium carbonate. The pale yellow, four-sided prisms lose ammonium hydrosulphide when exposed to air. L. Staudenmaier said that the salt is completely decomposed when confined over sulphuric acid. J. J. Berzelius made pale yellow, amorphous **lithium sulphotellurite,** presumably Li_6TeS_5, by saturating a soln. of lithium carbonate in tellurous acid with hydrogen sulphide, and evaporating the filtered liquid in vacuo. It decomposes easily in air. He also prepared **sodium sulphotellurite,** Na_6TeS_5, in an analogous way; and A. Gutbier and F. Flury, as indicated above, prepared $Na_2TeS_3.2H_2S$, by the action of hydrogen sulphide on a soln. of sodium tellurate. J. J. Berzelius obtained pale yellow, four-sided prisms of **potassium sulphotellurite,** K_6TeS_5, by an analogous process. The salt readily fuses to a black liquid which, on cooling, forms a yellowish-brown solid, soluble in water. The salt blackens in moist air, and dil. aq. soln. are also quickly decomposed on exposure to air. The **copper sulphotellurite,** Cu_3TeS_5, is obtained by double decomposition as a brown precipitate; similarly black **silver sulphotellurite,** Ag_6TeS_5, is produced by double decomposition. It is decomposed by heat into silver telluride, etc. By boiling calcium sulphide with tellurium disulphide and water, and evaporating the filtrate, a non-crystalline mass of **calcium sulphotellurite** is produced which decomposes rapidly on exposure to air; similarly with **strontium sulphotellurite,** which forms a pale yellow, unstable solid which is completely soluble in water; while **barium sulphotellurite** furnishes pale-yellowish four-sided prisms, fairly stable in air, which are slowly dissolved by water. By adding barium sulphotellurite to a soln. of magnesium sulphate, and evaporating the filtrate **magnesium sulphotellurite** is formed as a pale yellow crystalline mass soluble in water and alcohol, similarly with **zinc sulphotellurite,** which is at first light yellow and then turns brown; and **cadmium sulphotellurite** is formed similarly; whilst **mercurous sulphotellurite** furnishes a dark brown precipitate which decomposes with a hissing noise when heated, and giving off mercury forms yellowish-brown **mercuric sulphotellurite** which decomposes into sulphur and mercury telluride when strongly heated. When an aq. soln. of a cerous salt is treated with potassium sulphotellurite, cerium sulphotellurite is precipitated; it is brownish-yellow at first but soon becomes brownish-black. I. Pouget could not prepare *telluroantimonites* analogous to the selenoantimonites. Antimony telluride does not dissolve in a hot soln. of potassium telluride or hydrotelluride; and tellurium is itself insoluble in alkali sulphides—*vide infra.* J. J. Berzelius prepared dark brown **bismuth sulphotellurite,** by a similar process, a brown precipitate of **stannous sulphotellurite,** and a dark brown precipitate of **stannic sulphotellurite.** According to A. Ditte, tellurium dissolves in boiling soln. of the alkali sulphides, but tellurium is deposited in crystals as the soln. cools. It forms no *alkali tellurosulphostannates* analogous to the seleno-sulphostannates. J. J. Berzelius obtained a dark brown precipitate of **lead sulphotellurite** by double decomposition. P. Saldau found that the system PbS–PbTe does not form a continuous isomorphous mixed series. J. J. Berzelius obtained a precipitate of **manganese sulphotellurite** by a similar process; likewise **ferrous sulphotellurite** appears to be formed as a black precipitate; **ferric sulphotellurite** in brown flakes; **cobalt sulphotellurite,** as a black precipitate and likewise also with **nickel sulphotellurite.** A dark yellow soln. of **platinum sulphotellurite** was produced by the action of potassium sulphotellurite on a soln. of platinum tetrachloride; in a few days, it deposits the sulpho-salt in dark blue flakes which turn black when dried.

J. B. Hannay[2] reported a supposed **arsenic sulphotellurite,** $As_2S_3.2TeS_2$, which was called **arsenotellurite.** It was said to occur in small brownish needles on arsenical iron pyrites. The complex mineral from Nagyag, called *Blättertellur*—foliated tellurium—was named **nagyagite** by W. Haidinger[3]—*vide supra.* It is the *aurum galena* of G. A. Scopoli; the *or gris lamelleux* of I. Eques a Born; the *elasmose* of F. S. Beudant; the *Nagyakererz* of A. G. Werner; the *Blättererz* of D. L. G. Karsten; and the *blatterine* of J. J. N. Huot. Analyses were reported by P. Berthier, R. Brandes, F. Folbert, W. Hanko, S. J. Kappel, M. H. Klaproth, G. A. Kenngott, C. F. Plattner, E. Priwoznik, P. Schönbein, W. Muthmann and E. C. Schröder, E. S. Simpson, and P. Sipöcz. The results show that although the mineral is a **lead gold sulphotellurantimonite,** no definite formula can be assigned to the mineral. The composition ranges from $Pb_{10}(Au,Ag)_2Sb_2Te_6S_{15}$ to $Pb_{17}(Au,Ag)_4Sb_4Te_{10}S_{18}$. The formula was discussed by A. K. Boldireff. The occurrence of nagyagite at Nagyag and Offenbanyer, Transylvania, was discussed by M. H. Klaproth, J. F. L. Hausmann, B. von Inkey, G. vom Rath, A. Schrauf, H. Höfer, F. R. von Hauer and G. Stache, F. Beyschlag, V. R. von Zepharovich, and E. von Fellenberg and B. von Cotta; in Hungary, by F. von Richthofen, J. D. Dana, and A. des Cloizeaux. The *silberphyllinglanz* of A. Breithaupt, named *nobilite* by M. Adam, occurs at Deutsch-Pilsen, Hungary. A. Breithaupt called an auriferous variety of nagyagite, *edler Molybdänglanz.* The occurrence of nagyagite in North Carolina was described by F. A. Genth, and J. D. Dana; in Virginia, by G. A. Kenngott; in New Zealand, by J. Park; and in West Australia, by E. S. Simpson. According to J. C. L. Schröder van der Kolk, the streak of dark lead-grey mineral has a brownish tinge. The mineral occurs in granular or foliated masses, or in thin, flexible plates which, according to A. Schrauf, belong to the rhombic system, having the axial ratios $a:b:c=0{\cdot}2897:1:0{\cdot}2761$. The (010)-faces may be striated; and the (010)-cleavage perfect. The crystals were described by W. Phillips, W. H. Miller, J. D. Dana, and L. Fletcher; J. R. Blum described pseudomorphs of copper pyrites after nagyagite. The sp. gr. given by L. Sipöcz is 7·4613; by W. Hanko, 7·347; and by W. Petz, 7·22. The hardness is over 1·0. J. Joly found nagyagite gives a sublimate of tellurium monoxide between 440° and 525°; and of the dioxide at 610°. A. de Gramont described the spark spectrum; F. Beijerinck, and R. G. Harvey said that it is a good electrical conductor; and E. T. Wherry, that it is a poor radio-detector. For **bismuth sulphoditellurite,** Bi_2STe_2, *vide supra,* tetradymite.

A. Oppenheim reported that salts of the hypothetical *sulphotelluric acid,* H_2TeS_4, can be prepared as **sulphotellurates;** thus, by passing hydrogen sulphide into a soln. of sodium tellurate, and adding sodium hydroxide, the precipitated tellurium trisulphide passes into soln., and the liquid after saturating it again with hydrogen sulphide, furnishes sulphur-yellow, needle-like crystals of **sodium sulphotellurate,** Na_2TeS_4. The formation of the salt is represented by the equation: $2Na_2TeO_4+7H_2S=Te+3S+Na_2TeS_4+2NaOH+6H_2O$; similarly with **potassium sulphotellurate,** K_2TeS_4. The aq. soln. can be boiled without decomposition. L. Staudenmaier said that it is probable that in alkaline soln., the telluric acid is reduced by hydrogen sulphide so that the alleged sulphotellurates are really sulphotellurites. A. Gutbier and F. Flury could not prepare alkali sulphotellurates, and stated that with alkali tellurates, hydrogen sulphide gives no product approximating $Na_2TeS_3.2H_2S$.

REFERENCES.

[1] J. J. Berzelius, *Schweigger's Journ.*, **6**. 311, 1812; **34**. 78, 1823; *Pogg. Ann.*, **28**. 392, 1833; **32**. 1, 577, 1834; A. Ditte, *Compt. Rend.*, **95**. 641, 1882; F. Becker, *Liebig's Ann.*, **180**. 260, 1876; L. Staudenmaier, *Untersuchungen über das Tellur*, Leipzig, 1895; *Zeit. anorg. Chem.*, **10**. 197, 1895; A. Gutbier, *Studien über das Tellur*, Leipzig, 1901; *Zeit. anorg. Chem.*, **32**. 292, 1902; A. Gutbier and F. Flury, *ib.*, **32**. 272, 1902; M. Chikashige, *ib.*, **72**. 109, 1911; W. O. Snelling, *Journ. Amer. Chem. Soc.*, **34**. 802, 1912; A. M. Hageman, *ib.*, **41**. 329, 1919; F. M. Jäger, *Proc. Amsterdam Acad.*, **12**. 602, 1910; R. Astfalk, *Untersuchungen über kolloides Bor, Silizium und Tellurdisulfid*, Stuttgart, 1913; R. W. E. MacIvor, *Chem. News*, **87**. 209, 1903; H. Rose, *Pogg. Ann.*, **112**. 316, 1861; B. Brauner, *Journ. Chem. Soc.*, **55**. 382, 1889; **67**. 527, 549, 1895; *Sitzber. Akad. Wien*, **98**. 456, 1889; *Monatsh.*, **10**. 413, 1889; **12**. 34, 1891; *Zeit. anorg. Chem.*, **32**. 378, 1902; A. Oppenheim, *Beobachtungen über das Tellur und einige seiner Verbindungen*, Göttingen, 1859; *Journ. prakt. Chem.*, (1), **71**. 278, 1857; L. Losana, *Gazz. Chim. Ital.*, **53**. i, 396, 1923; L. Amaduzzi and M. Padoa, *Nuovo Cimento*, (6), **3**. i, 66, 1912; G. Pellini, *Atti Accad. Lincei*, (5), **18**. 1, 701, 1909; (5), **18**. ii, 19, 1909; A. Stock and P. Praetorius, *Ber.*, **47**. 131, 1914; I. Pouget, *Recherches sur les sulfo- et les selenio-antimonites*, Paris, 1899; *Ann. Chim. Phys.*, (7), **18**. 561, 1899; P. Saldau, *Ann. Inst. Mines St. Petersburg*, **4**. 228, 1913.

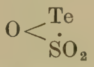
[2] J. B. Hannay, *Journ. Chem. Soc.*, **26**. 989, 1873.

[3] W. Haidinger, *Handbuch der bestimmenden Mineralogie*, Wien, 566, 1845; J. J. N. Huot, *Manuel de minéralogie*, Paris, **1**. 185, 1841; F. S. Beudant, *Traité élémentaire de minéralogie*, Paris, **2**. 539, 1832; I. Eques a Born, *Catalogue méthodique et raisonné de la collection des fossiles de Mlle. Eleonore de Raab*, Wien, 1790; *Lythophylacium Bornianum*, Praque, **1**. 68, 1772; G. A. Scopoli, *Ann. Hist. Nat.*, **3**. 107, 1777; A. G. Werner, *Berg. Journ.*, **2**. 373, 1789; V. R. von Zepharovich, *Mineralogisches Lexicon für das Kaiserthum Oesterreich*, Wien, 283, 1859; 214, 1873; W. H. Miller, *Introduction to Mineralogy*, London, 138, 1852; J. D. Dana, *A System of Mineralogy*, New York, 85, 1868; 106, 1892; J. R. Blum, *Die Pseudomorphosen des Mineralreichs*, Stuttgart, 262, 1863; G. A. Kenngott, *Uebersichte der Resultate mineralogischer Forschungen*, Wien, 143, 1851; D. L. G. Karsten, *Mineralogische Tabellen*, Berlin, 56, 1800; M. H. Klaproth, *Beiträge zur chemischen Kenntniss der Mineralkörper*, Berlin, **3**. 32, 1802; M. Adam, *Tableau minéralogique*, Paris, 35, 1869; J. F. L. Hausmann, *Handbuch der Mineralogie*, Göttingen, 133, 1813; C. F. Plattner, *Die Probirkunst mit dem Löthrohe*, Leipzig, 421, 1853; E. von Fellenberg and B. von Cotta, *Erzlagerstätten Ungarns und Siebenbürgens*, Leipzig, 173, 1861; B. von Cotta, *Berg. Hütt. Ztg.*, **20**. 190, 1861; W. Phillips, *Introduction to Mineralogy*, London, 246, 1819; 328, 1823; A. Schrauf, *Zeit. Kryst.*, **2**. 210, 239, 1878; L. Sipöcz, *ib.*, **11**. 211, 1885; *Tschermak's Mitt.*, (2), **7**. 269, 1886; H. Höfer, *Jahrb. geol. Reichsanst. Wien*, **17**. 1, 1866; F. von Richthofen, *ib.*, **11**. 253, 1860; F. Beyschlag, *Zeit. prakt. Geol.*, **4**. 464, 1896; G. vom Rath, *Sitzber. Niederrh. Ges. Bonn.*, 74, 201, 1876; *Vöröspatak und Nagyag im Siebengebürg*, Bonn, 1876; F. A. Genth, *The Minerals of North Carolina*, Washington, **26**. 1891; S. J. Kappel, *Viertelj. prakt. Pharm.*, **8**. 345, 1859; *Chem. Jahresb.*, 770, 1859; J. Joly, *Phil. Mag.*, (6), **27**. 1, 1914; F. R. von Hauer and G. Stache, *Geologie Siebenbürgens*, Wien, 1863; B. von Inkey, *Nagyag*, Budapest, 1885; A. des Cloizeaux, *Manuel de minéralogie*, Paris, **2**. 307, 1893; A. Breithaupt, *Vollständige Charakteristik des Mineralsystem*, 273, 1832; *Schweigger's Journ.*, **50**. 178, 1828; R. Brandes, *ib.*, **35**. 489, 1821; J. Park, *Proc. Australasian Assoc.*, **3**. 150, 1891; W. Petz, *Pogg. Ann.*, **57**. 477, 1842; L. Fletcher, *Phil. Mag.*, (5), **9**. 188, 1880; P. Schönbein, *Journ. prakt. Chem.*, (1), **60**. 166, 1853; *Liebig's Ann.*, **86**. 201, 1853; F. Folbert, *Verh. Siebenbürg. Ver. Naturwiss.*, **8**. 99, 1857; W. Hanko, *Math. Term. Tud. Ert.*, **6**. 340, 1886; E. Priwoznik, *Vorkommen von Tellur und Gewinnung aus seinen Erzen*, Wien, 1893; *Oesterr. Zeit. Berg. Hütt.*, **45**. 219, 1895; E. C. Schröder, *Zur Kenntniss der Verbindungen des Selens und des Tellurs*, Fürth, 1898; W. Muthmann and E. C. Schröder, *Zeit. anorg. Chem.*, **14**. 432, 1897; E. S. Simpson, *Bull. West Australian Geol. Sur.*, 42, 1912; W. M. Davy and C. M. Farnham, *Microscopic Examination of Ore Minerals*, New York, 98, 1920; J. C. L. Schröder van der Kolk, *Centr. Min.*, 78, 1901; F. Beijerinck, *Neues Jahrb. Min. B.B.*, **11**. 439, 1897; A. de Gramont, *Bull. Soc. Min.*, **18**. 355, 1895; *Analyse spectrale directe des minéraux*, Paris, 1895; E. T. Wherry, *Amer. Min.*, **10**. 30, 1925; P. Berthier, *Ann. Chim. Phys.*, (2), **51**. 150, 1832; A. Breithaupt, *Vollständige Characteristik des Mineralsystems*, Dresden, 233, 273, 1832; A. K. Boldireff, *Centr. Min.*, 193, 1924; R. G. Harvey, *Econ. Geol.*, **23**. 778, 1928.

§ 15. Tellurium Oxysulphides and Sulphates

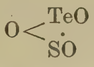
R. Weber,[1] and E. Divers and M. Shimose found that when sulphur trioxide reacts with tellurium, **tellurium sulphotrioxide,** $TeSO_3$, is formed. The two substances may remain in contact for a short time without reaction, and for a longer time if the mixture is cold. There is an evolution of heat, and the reaction is completed a few minutes after it has started. The excess of sulphur trioxide remains colourless; the sulphotrioxide is a bulky, deep red solid. After the sulphotrioxide had been digested in the liquid trioxide at 30°–40° for some time, the liquid was drained off and the adherent trioxide was removed by heating it to 35° in vacuo, and the trioxide absorbed by means of borax—potassium hydroxide as absorbent acts too violently. E. Divers and M. Shimose made the sulphotrioxide by the action of hydrogen telluride on a soln. of tellurium dioxide in conc. sulphuric acid: $2H_2Te+TeO_2+3H_2SO_4=3TeSO_3+5H_2O$; by the action of conc. sulphuric acid on tellurium monoxide: $2TeO+3H_2SO_4=TeSO_3+Te(SO_4)_2+3H_2O$. The red colour of a soln. of tellurium in fuming or conc. sulphuric acid—noticed by M. H. Klaproth, A. Hilger, A. C. Schultz-Sellack, F. J. Müller von Reichenstein, H. G. Magnus, F. von Kobell, H. Rose, J. J. Berzelius, and N. W. Fischer—was attributed by R. Weber, and E. Divers and M. Shimose to the presence of tellurium sulphotrioxide, and W. Prandtl and P. Borinsky obtained the sulphotrioxide by the action of chlorosulphonic acid on tellurium. N. W. Fischer said that the red colour appears when one part of tellurium is present in 2000 parts of acid; no sulphur dioxide is evolved as the red coloration is produced. If the red soln. is heated, the red colour disappears, tellurium sulphate is formed, and sulphur dioxide is given off. E. Moles studied the f.p. and conductivity of a soln. of tellurium in sulphuric acid, and obtained abnormal values for the mol. wt. R. Auerbach found that tellurium dissolves in pyrosulphuric acid as single atoms; and on coagulation by dilution with water, the colour changes from red, through violet, to blue as the metal is precipitated—*cf.* selenium oxysulphate.

According to R. Weber, and E. Divers and M. Shimose, at ordinary temp. tellurium sulphotrioxide is an amorphous solid, which softens without melting at about 30°. It is of a beautiful red colour, and transparent in very thin layers. It is finely vesiculated in consequence of the vaporization within its substance of the excess of sulphur trioxide at first mixed with it. R. Weber said that it is very unstable, decomposing even in sealed tubes at ordinary temp. yielding sulphur dioxide, but E. Divers and M. Shimose observed it to be quite stable at ordinary temp. in the closed tube when pure, neither changing colour nor evolving sulphur dioxide. During its preparation and purification, also, no sulphur dioxide was produced, when the sulphur trioxide was quite anhydrous. The sulphotrioxide does, indeed, sometimes slowly decompose when left in the crude state, its red colour assuming a brown shade, and then, too, sulphur dioxide is formed. E. Divers and M. Shimose also observed that when red tellurium sulphotrioxide is heated sufficiently, its colour changes to a bright fawn-brown. Prolonged heating in a vacuum even at 35° effects this change, but so very slowly that no change can be perceived, even after the lapse of an hour. At higher temp. the transformation is more rapid, and at 90°, almost instantaneous. No gas is evolved, and nothing but the striking change of colour is observable. The vesicular condition remains just as it was, even to the iridescence of the superficial vesicles. Heated to 130°, it softens and shrinks, as the vesicular structure collapses. Its brown colour is now of a deeper shade, owing to the absence of the vesicles. Heated to 180°, it again changes colour, and again becomes vesiculated, this time from evolution of sulphur dioxide. The mass eventually becomes black and solid on further heating, and now consists of the tellurium monoxide, the decomposition being almost complete at about 230°. The earlier effects of heating the red sulphotrioxide under atm. press. do not appear to differ essentially from those of heating in vacuo. The brown sulphotrioxide remains unaffected when digested with liquid sulphur trioxide, but like the red sulphotrioxide it dissolves readily in sulphuric acid, without evolution of sulphur dioxide, and yields the usual deep amethyst-red soln. In its behaviour with water, no difference from the red sulphotrioxide has been observed, if we except a somewhat more violent action in the case of the red, perhaps due to the presence of a little sulphur trioxide in the preparation so tested. If water be passed into the red soln. of tellurium in sulphuric acid, the tellurium is all precipitated; and tellurium sulphotrioxide is decomposed by water $TeSO_3+H_2O=Te+H_2SO_4$, but some tellurium monoxide is formed (*q.v.*): $TeSO_3+H_2O=H_2SO_3+TeO$, followed by $2TeO+H_2O=Te+H_2TeO_3$; or collectively $2TeSO_3+3H_2O=Te+H_2TeO_3+2H_2SO_3$. These equations, said E. Divers and M. Shimose, "do not make at all clear the production of excess of tellurium, and that of the sulphuric acid remains inexplicable, since sulphurous acid has no reducing action upon tellurous acid either alone or in the presence of sulphuric acid, hydrochloric acid being required. Nor is the constitution clear. If the sulphoxide is a sulphite, it is strange that it should dissolve in sulphuric acid without giving off sulphurous acid. Further, if it is a sulphite, it should be in the same series of tellurium compounds as tellurium monoxide, and there should be a corresponding hypotellurous sulphate, SO_4Te, formed from tellurium monoxide and sulphuric acid, which is not the case. They suggested the formulæ:



$$O{<}\genfrac{}{}{0pt}{}{Te}{SO_2}$$

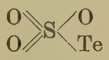
Red sulphotrioxide.



$$O{<}\genfrac{}{}{0pt}{}{TeO}{SO}$$

Brown sulphotrioxide.

which represent the red modification as a sulphonate of tellurium in the unstable condition of bivalency, and the brown modification as a better balanced combination of oxides of the two elements, in which both are quadrivalent, and the combination, therefore, more stable under rise of temp. than the red modification, and yet a combination out of which the tellurium cannot be expected to separate from the sulphur without reduction at the same time to a state of lower valency." R. Auerbach said that tellurium dissolves as Te-mols. in pyrosulphuric acid. W. Prandtl and P. Borinsky, by analogy with their hypothesis for sulphur sesquioxide, represented the constitution of tellurium sulphotrioxide:



Vide the action of tellurium on selenic acid. According to C. A. Cameron and J. Macallan, coloured compounds produced by the action of sulphur, selenium, and tellurium on selenic acid have been produced by the action of these elements on sulphuric acid or anhydride to form the compounds SSO_3, $SeSO_3$, and $TeSO_3$. Owing to their similarity in the modes of formation with those formed by selenic acid, it is assumed that the resulting *selenotrioxides* are analogous to the *sulphotrioxides* in which selenium and sulphur are mutually replaceable. The two series of compounds are:

	Sulphotrioxides.	Selenotrioxides.
Blue	SSO_3	$SSeO_3$
Green	$SeSO_3$	$SeSeO_3$
Red	$TeSO_3$	$TeSeO_3$

The colour of the above compounds appears to be almost entirely due to the element which is added on to the anhydride; the sulphur or selenium in the residual portion of the mol. has scarcely any effect upon the colour.

J. J. Berzelius[2] evaporated a soln. of tellurium in conc. sulphuric acid, and obtained what he regarded as the normal sulphate; but D. Klein and J. Morel showed that the product is probably a basic salt, **telluryl oxysulphate,** $2TeO_2.SO_3$; or $Te_2O_3(SO_4)$; or $O=(TeO)_2=SO_4$. B. Brauner obtained this product by boiling tellurium dioxide with sulphuric acid (1 : 1), and cooling the soln. D. Klein and J. Morel, P. Köthner, and R. Metzner used a more dil. acid, and evaporated the soln. for crystallization. B. Brauner said that if less than 50 per cent. sulphuric acid is used, tellurium dioxide separates from the soln. J. J. Berzelius, A. Gutbier, and E. Divers and M. Shimose obtained the salt from a soln. of tellurium in hot sulphuric acid. The salt furnishes rhombic prismatic crystals, which, according to K. Vrba, have the axial ratios $a:b:c=0·5265:1:0·7860$; the (001)-cleavage is complete; complex twinning occurs about the (110)-plane. The crystals produced by the slow cooling of the sulphuric acid soln. are colourless six-sided prisms; and those obtained by rapid cooling are microscopic, six-sided plates. The sp. gr. of the tabular crystals is 4·605, and that of the prismatic crystals 4·7. R. Metzner found that the crystals are non-hygroscopic, and stable. No decomposition occurs at 440°, but at 500°, a little decomposition occurs. Hence it is easy to separate adherent sulphuric acid from the crystals, by heating them in vacuo. J. J. Berzelius said that the salt melts when heated, and at a higher temp. gives off sulphur trioxide leaving a residue of tellurium dioxide; cold water acts slowly on the salt, and hot water transforms it completely into tellurium dioxide and sulphuric acid. It dissolves in warm hydrochloric and nitric acids, and separates on cooling the hot, sat. soln. R. Metzner utilized the properties of this sulphate for the separation of selenium and tellurium. F. Ephraim prepared **tellurium hexamminosulphate,** $TeSO_4.6NH_3$.

R. Metzner prepared **ammonium sulphatotellurite,** $(NH_4)HSO_4.2TeO_2.SO_3.2H_2O$, by adding ammonium sulphate to a soln. of telluryloxysulphate in hot, dil. sulphuric acid; on cooling, acicular crystals separate out. He also prepared **potassium sulphatotellurite,** $KHSO_4.2TeO_2.SO_3.2H_2O$, in a similar manner. G. Pellini observed that **rubidium hydrosulphatohydrotellurate,** $Rb(HSO_4)(HTeO_4)$, may be formed—*vide supra,* hydrotellurates. F. Förster and co-workers observed no sign of the possible formation of *tellurothiosulphuric acid,* or tellurodithionic acid corresponding with the corresponding selenium compounds (*q.v.*). W. Prandtl and P. Borinsky obtained **tellurium hexoxydisulphotetrachloride,** $TeCl_4.2SO_3$, by the action of pyrosulphuryl chloride on tellurium; or of sulphur trioxide on tellurium tetrachloride. The complex melts in vacuo at 85°; and at 120° in vacuo it furnishes **tellurium trioxysulphotetrachloride,** $TeCl_4.SO_3$. It was also found that sulphur trioxide reacts with tellurium tetrabromide and **tellurium heptoxydisulphodibromide,** $TeOBr_2.2SO_3$, is formed.

References.

[1] R. Weber, *Journ. prakt. Chem.* (2), **25**. 218, 1882; *Pogg. Ann.*, **156**. 531, 1875; N. W. Fischer, *ib.*, **10**. 491, 1827; **12**. 153, 1828; **14**. 328, 1828; **15**. 77, 1829; **16**. 118, 1829; W. Prandtl and P. Borinsky, *Zeit. anorg. Chem.*, **62**. 237, 1909; P. Borinsky, *Ueber die Einwirkung von Schwefeltrioxyd und dessen Chlorsubstitutionsprodukten auf Schwefel, Selen und Tellur*, München, 1909; A. Hilger, *Liebig's Ann.*, **171**. 211, 1874; *Sitzber. Phys. Med. Soc. Erlangen*, **6**. 89, 1874; R. Auerbach, *Zeit. phys. Chem.*, **121**. 337, 1926; H. Rose, *Ausführliches Handbuch des analytischen Chemie*, Braunschweig, **1**. 411, 1851; A. C. Schultz-Sellack, *Ber.*, **4**. 113, 1871; *Journ. Pharm. Chim.*, (4), **15**. 250, 1872; E. Moles, *Anal. Fis. Quim.*, **13**. 134, 1915; H. G. Magnus, *Dissertatio de tellurio*, Berolensis, 1827; *Pogg. Ann.*, **17**. 521, 1829; M. H. Klaproth, *Mem. Akad. Berlin*, **50**. 17, 1798; *Beiträge zur chemischen Kenntniss der Mineralkörpen*, Berlin, **3**. 1, 1802; London, **2**. 1, 1804; *Crell's Ann.*, **1**. 91, 1798; *Gilbert's Ann.*, **12**. 246, 1802; F. J. Müller von Reichenstein, *Phys. Arb. Freunde Wien*, **1**. 1, 1782; **3**. 48, 1785; J. J. Berzelius, *Schweigger's Journ.*, **6**. 311, 1812; **34**. 78, 1823; *Pogg. Ann.*, **28**. 392, 1833; **32**. 1, 577, 1834; F. von Kobell, *Ann. Gelehrte München*, **46**. 302, 1857; E. Divers and M. Shimose, *Journ. Chem. Soc.*, **44**. 323, 1883; **46**. 201, 1884; C. A. Cameron and J. Macallan, *Proc. Roy. Soc.*, **46**. 32, 1890; *Monit. Scient.*, (4), **3**. 1036, 1889; *Chem. News*, **59**. 219, 232, 258, 269, 1889; F. Förster, F. Lange, O. Drossbach and W. Seidel, *Zeit. anorg. Chem.*, **128**. 245, 1923; R. Auerbach, *Koll. Zeit.*, **38**. 343, 1926; *Zeit. phys. Chem.*, **121**. 337, 1926; E. Priwoznik, *Oesterr. Zeit. Berg. Hütt.*, **45**. 219, 1897; *Vorkommen von Tellur und Gewinnung aus seinen Erzen*, Wien, 1893.

[2] J. J. Berzelius, *Schweigger's Journ.*, **6**. 311, 1812; **34**. 78, 1823; *Pogg. Ann.*, **28**. 392, 1833; **32**. 1, 577, 1834; F. Ephraim, *Ber.*, **59**. B, 1219, 1926; P. Köthner, *Zeit. anorg. Chem.*, **34**. 402, 1903; *Liebig's Ann.*, **319**. 1, 1901; *Das reine Tellur und sein Atomgewicht*, Halle, 1901; R. Metzner, *Compt. Rend.*, **126**. 1716, 1898; *Ann. Chim. Phys.*, (7), **15**. 203, 1898; *Sur quelques composés du sélénium et du tellure*, Paris, 1898; B. Brauner, *Journ. Chem. Soc.*, **55**. 382, 1889; **67**. 527, 548, 1895; *Sitzber. Akad. Wien*, **98**. 456, 1889; *Monatsh.*, **10**. 443, 1889; **12**. 34, 1891;

A. Gutbier, *Studien über das tellur*, Leipzig, 1901; *Zeit. anorg. Chem.*, **32**. 31, 1902; D. Klein and J. Morel, *Ann. Chim. Phys.*, (6), **5**. 78, 1885; K. Vrba, *Zeit. Kryst.*, **19**. 5, 1891; E. Divers and M. Shimose, *Journ. Chem. Soc.*, **44**. 323, 1883; **46**. 201, 1884; G. Pellini, *Atti Accad. Lincei*, (5), **18**. ii, 279, 1909; W. Prandtl and P. Borinsky, *Zeit. anorg. Chem.*, **62**. 237, 1909; P. Borinsky, *Ueber die Einwirkung von Schwefeltrioxyd und dessen Chlorsubstitutionsprodukten auf Schwefel, Selen und Tellur*, München, 1909; F. Förster, J. Lange, O. Drossbach and W. Seidel, *Zeit. anorg. Chem.*, **128**. 245, 1923.

§ 16. Tellurium Nitrates

M. H. Klaproth,[1] and J. J. Berzelius found that tellurium is readily dissolved by nitric acid forming a colourless soln. D. Klein and J. Morel's observations on this subject have been discussed in connection with tellurium itself. With an acid of sp. gr. 1·15, the evaporation of the soln. at about 50° furnishes, according to J. F. Norris and co-workers, and P. Köthner, **telluryl oxyhydroxynitrate,** $Te_2O_3(OH)(NO_3)$, that is, $HO{-}TeO{-}O{-}TeO{-}NO_3$. P. Köthner said that the formula $4TeO_2.N_2O_5.1{\cdot}5H_2O$ is not correct. According to P. Köthner, the salt is best prepared by dissolving tellurium in a slight excess of nitric acid; and evaporating the liquid so as to obtain crystals from the hot soln. The crystals are washed with warm nitric acid of sp. gr. 1·255, and then with colder acid; and then with acid at 5°, then with a 3 : 1-mixture of cold nitric acid and absolute alcohol; then gradually raising the proportion of alcohol until finally alcohol alone is used to remove the last trace of nitric acid. The crystals are then dried in vacuo over phosphorus pentoxide. P. Köthner obtained the crystals as rhombic prisms from hot soln. J. F. Norris and co-workers said that the crystals are not hygroscopic, and do not lose their lustre when exposed to air, but in moist air, P. Köthner found that tellurous and nitric acids are formed. The salt is not changed when kept in vacuo over calcium chloride. J. F. Norris and co-workers said that the nitrate suffers no loss in weight from 110° to 170°, but at 190° the crystals begin to lose nitrogen oxide; and tellurium dioxide is formed at 300°. According to D. Klein and J. Morel, the basic nitrate is slowly decomposed by cold water, nitric acid and a small proportion of tellurium dioxide is dissolved, while rectangular plates of tellurium dioxide remain. At a higher temp., decomposition is almost instantaneous; the soln. becomes strongly acid, and the greater part of the tellurium dioxide remains undissolved in the form of microscopic octahedra. These facts explain the commonly-accepted statement that tellurium dioxide is slightly soluble in water, but does not redden blue litmus. The basic nitrate does not act on moistened litmus in the cold until after several hours, and when decomposition takes place the soln. of a small quantity of tellurium dioxide is due to the presence of the free nitric acid. Basic tellurium nitrate dissolves in nitric acid and crystallizes readily when the soln. is concentrated and cooled. It seems to be much more soluble in the dil. than in the conc. acid. Soln. in nitric acid of sp. gr. 1·1–1·4 are stable at all temp. and soln. in acid of sp. gr. about 1·35, are not decomposed on addition of 100 vols. of water. On the other hand, soln. in nitric acid of sp. gr. 1·1 are decomposed by water with precipitation of tellurium dioxide, decomposition being more rapid the greater the proportion of water. The limit of decomposition appears to be reached when the soln. is mixed with 5 vols. of water; under these conditions, the precipitation of tellurium dioxide is very slow, and with a smaller proportion of water no decomposition takes place. The tellurium dioxide deposited when the nitric acid soln. are diluted, does not crystallize in octahedra, but in some perfectly distinct form.

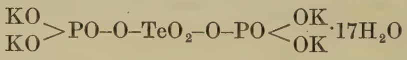
A. Rosenheim and G. Jander found that soln. containing telluric acid and potassium nitrate deposit large crystals of **potassium dinitratotellurate,** $2KNO_3.H_6TeO_6.2H_2O$; and they can be recrystallized from dil. soln. of potassium nitrate without decomposition. Similarly, with soln. of silver nitrate, crystals of **silver nitratotellurate,** $AgNO_3.H_6TeO_6$, were formed. They attributed the formation of these complexes to the weak acid nature of telluric acid. A. Oppenheim also obtained silver nitratotellurate as a precipitate by adding silver nitrate to a soln. of telluric acid ; similarly with **mercurous nitratotellurate,** and with **lead nitratotellurate.**

REFERENCES.

[1] J. F. Norris, H. Fay and D. W. Edgerly, *Amer. Chem. Journ.*, **23**. 105, 1900 ; P. Köthner, *Zeit. anorg. Chem.*, **34**. 402, 1903 ; *Liebig's Ann.*, **319**. 1, 1901 ; *Das reine Tellur und sein Atomgewicht*, Halle, 1901 ; J. J. Berzelius, *Schweigger's Journ.*, **6**. 311, 1812 ; **34**. 78, 1823 ; *Pogg. Ann.*, **28**. 392, 1833 ; **32**. 1, 577, 1834 ; M. H. Klaproth, *Mem. Akad. Berlin*, **50**. 17, 1798 ; *Beiträge zur chemischen Kenntniss der Mineralkörpen*, Berlin, **3**. 1, 1802 ; London, **2**. 1, 1804 ; *Crell's Ann.*, **1**. 91, 1798 ; *Gilbert's Ann.*, **12**. 246, 1802 ; A. Oppenheim, *Beobachtungen über das Tellur und einige seiner Verbindungen*, Göttingen, 1859 ; *Journ. prakt. Chem.*, (1), **71**. 278, 1857 ; D. Klein and J. Morel, *Compt. Rend.*, **99**. 540, 567, 1884 ; *Bull. Soc. Chim.*, (2), **43**. 204, 1885 ; A. Gutbier, *Sitzber. phys. Med. Soc. Erlangen*, **37**. 292, 1905 ; *Studien über das Tellur*, Leipzig, 1901 ; A. Rosenheim and G. Jander, *Koll. Zeit.*, **22**. 23, 1918 ; G. Jander, *Ueber die Tellursäure und ihre Alkalisalze in ihrem Verhalten als Halbkolloide*, Berlin, 1917.

§ 17. Tellurium Phosphates

J. J. Berzelius,[1] and H. Rose observed that when a soln. of sodium phosphate is added to a neutral or feebly acid soln. of tellurous acid a white precipitate is formed ; and D. Klein found that the spontaneous evaporation of a soln. of tellurous acid in conc. phosphoric acid furnishes pulverulent *tellurium phosphate* which cannot be washed with water because it is resolved by that liquid into tellurium dioxide and phosphoric acid. The product contains a variable proportion of phosphoric acid. F. Ephraim and E. Majler were unable to prepare an ammonium phosphotellurate analogous to the phosphoselenates. According to R. F. Weinland and H. Prause, telluric acid forms compounds with phosphates analogous with those obtained with the arsenates, thus, **ammonium diphosphatotellurate,** $2(NH_4)_2O.P_2O_5.TeO_3.4H_2O$, that is, $\{(NH_4O)_2{=}PO\}_2TeO_2$, was obtained by evaporating a soln. of 2 mols of phosphoric acid, a mol of orthotelluric acid, and 4 mols of ammonia. The four-sided plates belong to the triclinic system, and have the axial ratios $a:b:c=0\cdot7337:1:0\cdot7698$, and $\alpha=90° \, 28'$, $\beta=96° \, 42'$, and $\gamma=91° \, 34'$. The salt is easily soluble in water, and the soln. has an alkaline reaction ; it can be recrystallized from water ; but it ought not to be warmed very much or ammonia will be given off. If the three components just indicated be in proportions between 2 : 1 : 2·5 and 4 : 1 : 6, **ammonium triphosphatotellurate,** $4(NH_4)_2O.3P_2O_5.2TeO_3.11H_2O$, or $\{NH_4O\text{–}PO(OH)\}_2TeO_2 : TeO(OH).PO(ONH_4)_2$, is produced in monoclinic prisms or plates with the axial ratios $a:b:c=0\cdot8097:1:0\cdot6347$, and $\beta=116° \, 25'$, with twinning about the (001)-plane. The crystals react acid ; they can be recrystallized from water ; and they do not effloresce over sulphuric acid. By evaporating slowly over sulphuric acid a soln. of 2 mols of phosphoric acid, one mol of orthotelluric acid, and 2 mols of sodium hydroxide, six-sided, bipyramidal crystals of **sodium phosphatotellurate,** $2Na_2O.P_2O_5.2TeO_3.9H_2O$, or $(NaO)_2PO.O.TeO_2(OH)$, are formed. The salt cannot be recrystallized from water without decomposition. The hexagonal crystals have the axial ratio $a:c=1:1\cdot3646$; they do not effloresce over sulphuric acid ; they are sparingly soluble in cold water ; the aq. soln. is slightly alkaline towards litmus. R. F. Weinland and H. Prause prepared **potassium hydrodiphosphatotellurate,** $1\frac{1}{2}K_2O.P_2O_5.TeO_3.17\frac{1}{2}H_2O$, or



$$\begin{matrix}KO\\KO\end{matrix}{>}PO\text{–}O\text{–}TeO_2\text{–}O\text{–}PO{<}\begin{matrix}OK\\OK\end{matrix}\cdot 17H_2O$$

by the evaporation in vacuo over conc. sulphuric acid or at a temp. below 40°, of a soln. of theoretical proportions of the component salts. The acicular or prismatic crystals of the *heptadecahydrate* effloresce at ordinary temp., but are stable at 4° or 5°. The salt is soluble in water, and the aq. soln. reacts acidic. The salt loses all its water at 200° ; and over sulphuric acid, about three-fourths of the water is given off forming the *tetrahydrate*, $(KO)_2PO.O.TeO_2O.PO(OH)OK.6H_2O$. The same salt is produced as in the case of the heptadecahydrate using a conc. soln. of phosphoric acid, or a soln. of 4 mols of phosphoric acid, one mol of orthotelluric acid, and 5 mols of potassium hydroxide. The salt forms radiating aggregates of rhombic crystals which do not effloresce in the desiccator, and lose no water at 100°. The corresponding **rubidium hydrophosphatotellurate,** $(RbO)_2PO.O.TeO_2.O.PO(OH)ORb.4H_2O$, was obtained from a soln. of 4 mols of phosphoric acid, one mol of orthotelluric acid, and 6 mols of rubidium hydroxide.

For tellurium phosphotridecachloride, $2TeCl_4.PCl_5$, *vide supra.*

REFERENCES.

[1] J. J. Berzelius, *Schweigger's Journ.*, **6**. 311, 1812; **34**. 78, 1823; *Pogg. Ann.*, **28**. 392, 1833; **32**. 1, 566, 1834; H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, **1**. 411, 1851; R. F. Weinland and H. Prause, *Zeit. anorg. Chem.*, **28**. 45, 1901; H. Prause, *Ueber Verbindungen der Tellursäure mit Jodaten, Phosphaten, und Arsenaten*, Leipzig, 1901; F. Ephraim and E. Majler, *Ber.*, **43**. 277, 1910; D. Klein, *Ann. Chim. Phys.*, (6), **10**. 113, 1887.

CHAPTER LX

CHROMIUM

§ 1. The History and Occurrence of Chromium

In 1766, J. G. Lehmann[1] described *nova minera plumbi specie crystallina rubra* which he had obtained from Ekateribourg, Siberia, but for the next thirty years, the composition of the mineral was more or less conjectural. P. S. Pallas, indeed, said that it contained lead, sulphur, and arsenic. J. G. Wallerius called it *minera plumbi rubra ;* A. G. Werner, *rothes Bleierz ;* and L. C. H. Macquart, *plomb rouge de Sibérie—vide infra,* crocoite. J. J. Bindheim supposed the mineral to be a compound of molybdic acid, nickel, cobalt, iron, and copper. In 1794, L. N. Vauquelin in co-operation with L. C. H. Macquart, reported that it contained lead oxide, iron, alumina, and a large proportion—38 per cent.—of oxygen—*oxyde de plomb suroxygéne ;* but in 1797, L. N. Vauquelin, in his *Mémoire sur une nouvelle substance métallique, contenue dans le plomb rouge de Sibérie, et qu'on propose d'appeler chrome,* showed that the contained lead was united to a peculiar acid which was shown to be the oxide of a new metal to which he applied the name *chrom*—from χρῶμα, colour—*parce que ses combinaisons sont toutes plus ou moins colorées.* L. N. Vauquelin said :

> I observed that when the powdered mineral is boiled with a soln. of two parts of potassium carbonate, the lead combines with the carbonic acid, and the alkali, with the peculiar acid, to form a yellow soln. which furnishes a crystalline salt (potassium chromate) of the same colour. The mineral is decomposed by mineral acids, and when the soln. is evaporated it furnishes a lead salt of the mineral acid, and *l'acide du plomb rouge* (chromic acid) in long prisms the colour of the ruby. When the compound of *l'acide du plomb rouge* with potash is treated with mercury nitrate, it gives a red precipitate, the colour of cinnabar ; with lead nitrate, an orange-yellow precipitate ; with copper nitrate, a maroon-red, etc. *L'acide du plomb rouge,* free or in combination, dissolves in fused borax, microcosmic salt, or glass to which it communicates a beautiful emerald green colour.

L. N. Vauquelin isolated a pale-grey metal by heating a mixture of the chromic acid and carbon in a graphite crucible. About the same time as L. N. Vauquelin, M. H. Klaproth, in 1797, also demonstrated the presence of a new element in the red Siberian ore, but in a letter to *Crell's Annalen* he stated that L. N. Vauquelin had anticipated his discovery. M. H. Klaproth had dissolved the mineral in hydrochloric acid, and after crystallizing out the lead chloride, he saturated the liquid with sodium carbonate, and obtained the *Metallkalk.* He also noted the characteristic colour which it imparted to fused borax, and fused microcosmic salt. The results were confirmed by J. F. Gmelin, A. Mussin-Puschkin, S. M. Godon de St. Menin, and J. B. Richter. F. Brandenburg tried to show that the chromic acid of L. N. Vauquelin is really a compound of chromic oxide and one of the mineral acids, but K. F. W. Meissner, and J. W. Döbereiner proved this hypothesis to be untenable.

Chromium is widely diffused, but does not occur in the free state. F. W. Clarke[2] estimated that the igneous rocks of the earth's lithosphere contain 0·052 per cent. Cr_2O_3, 0·045 per cent. Cl, and 0·051 per cent. BaO. F. W. Clarke gave 0·37 per cent. Cr ; F. W. Clarke and H. S. Washington, 0·68 per cent. ; H. S. Washington gave 0·20 per cent.; G. Berg, 0·033 per cent.; and J. H. L. Vogt, 0·01 per cent. W. Vernadsky gave 0·0033 for the percentage amount, and 0·01 for the atomic proportion. F. W. Clarke and H. S. Washington estimated that the earth's 10-mile crust, the hydrosphere and atm. contained 0·062 per cent. Cr; and the earth's 25-mile crust, the hydrosphere and atm., 0·65 per cent. of Cr. W. and J. Noddack and O. Berg gave for the absolute abundance of the elements in the earth: Cr, 3×10^{-5}; and Fe, 10^{-2}; whilst A. von Antropoff obtained for the atomic percentages, 0·29 in stellar atmospheres; 0·021 in the earth's crust; 0·05 in the whole earth; and 0·29 in silicate meteorites. The subject was also discussed by V. M. Goldschmidt, G. Tamman, R. A. Sonder, P. Niggli, E. Herlinger, O. Hahn, J. Joly, and H. S. Washington. P. Pondal said that the proportion of chromium in basic rocks is greater than it is in acidic rocks where the proportion is very low or zero; he found 0·32 to 0·002 per cent. of Cr_2O_3 in 15 samples of Galician magmas.

Chromium occurs in minerals of extra-terrestrial origin. A. Laugier[3] found it in a meteorite from Vago. According to L. W. Gilbert, J. Lowitz had previously found chromium in a meteorite from Jigalowka, but the analysis was not published. Numerous analysis of other meteorites have been reported by E. Cohen, and others. J. N. Lockyer studied the spectra of meteorites. The general results show that chromium is a constant constituent of these meteorites. The amounts vary from 0·003 to 4·41 per cent. In most cases it is present as chromite; sometimes in the chondrite, olivine, pyroxene, pictotite, and *daubréeite*, $FeCr_2S_4$. H. A. Rowland,[4] T. Dunham and C. E. Moore, S. A. Mitchell, P. W. Merrill, H. Deslandres, G. Kirchhoff, J. N. Lockyer, and F. McClean, reported that the spectral lines of chromium appear in the solar or in stellar spectra. H. Deslandres also found chromium lines in the ultra-violet spectrum of the corona.

The principal mineral for the supply of chromium is *chromite*. It has a variety of names: *chrome ore, chrome-ironstone*, or *chrome iron ore*, $FeO.Cr_2O_3$, in which the iron and chromium are more or less replaced by magnesium and aluminium. Iron ore with up to about 3 per cent. of chromium is called *chromiferous iron ore*. The origin of the chromite deposits has been discussed by M. E. Glasser,[5] L. W. Fisher, E. Sampson, F. Ryba, C. S. Hitchin, J. S. Diller, P. A. Wagner, E. A. V. Zeally, J. H. L. Vogt, W. N. Benson, A. C. Gill, C. S. Ross, and J. T. Singewald. E. Sampson believed that although chromite may crystallize at a late stage as a magmatic mineral, a large proportion passes into a residual soln., or into a highly aq. soln. capable of considerable migration. The following analyses, Table I, were quoted by W. G. Rumbold:[6]

TABLE I.—ANALYSES OF CHROMITE ORES.

Locality.	Cr_2O_3.	FeO.	MgO.	Al_2O_3.	SiO_2.
Baluchestan . . .	57·0	13·6	16·6	9·8	1·2
Selukwe, Rhodesia . .	46·5	15·7	11·7	15·5	8·0
Canada	46·0	22·5	4·9	8·9	7·7
Urals, Russia . . .	55·8	21·6	13·9	3·3	5·4
Orsova, Hungary . . .	39·0	16·1	17·2	17·5	8·0
Asia Minor	60·1	15·7	16·4	6·3	1·1
California	43·7	14·0	16·5	16·0	8·0
North Carolina . . .	57·8	25·7	5·3	7·8	2·8
New Caledonia . . .	54·5	17·7	8·0	11·1	3·1

The commercial value of the ore is based on the proportion of contained chromic oxide. The ore may be sold per ton; or per unit of contained chromic oxide over, say, a 50 per cent. standard. Prior to the Great War, Rhodesia and New Caledonia were the chief producing countries; during the years of the war, and with the lack of facilities for ocean freights, there were marked increases in output from

United States, India, and Canada. The geographical distribution of chrome ore is illustrated in a general way by the map, Fig. 1.

Europe.—In the **United Kingdom,**[7] deposits are associated with the serpentine near Loch Tay, and on the Island of Unst, Shetland. In **Austria,**[8] the ore has been worked in the Gulse Valley, and in Styria; in **Hungary**, at Orsova,[9] there are low grade ores at Ogradina, Dubova, Placishevitsa, Tsoritza, and Eibenthal; and in **Serbia,**[10] near Cacak. In **Germany,**[11] there is a large deposit of chromite on the south side of Mount Zobten, Lower Silesia; the exploitation of the chromite near Frankenstein, Lower Silesia, has not been a commercial success. In **Italy,**[12] at Ziona. **Greece**[13] has been a steady producer of chromite for many years; there are important deposits at Volo, and Pharsala; there are deposits in the provinces of Salonika, Lokris, and Boitio; and on the islands of Euboea, and Skyros. E. Nowack,[14] and D. A. Wray described the deposits in Macedonia and **Albania.** In **Turkey,**[15] there are deposits of chrome iron ore. In **Norway,**[16] there are deposits at Trondhjem, and Röraas; those in **Sweden** were discussed by F. R. Tegengren.[17] In **Portugal,**[18] there is a deposit near Braganca; and in **Spain,**[19] near Huelva. **Russia**[20] is rich in chromite ore, and was formerly a large producer. Chrome ore is found associated with the soapstones and serpentines of the Ural Mountains—*e.g.* on the banks of the Kamenka and Fopkaja. Masses of chromite occur at Orenburg. In **Jugoslavia** chrome ore occurs at Ridjerstica in Serbia; and in the valleys of Dubostica, Tribia, and Krivaia in Bosnia.[21] Chromite also occurs at Raduscha, and the provinces of Kossovo and Monastir. P. Lepez,[22] E. Nowack, and D. A. Wray described the deposits of north-west **Macedonia.**

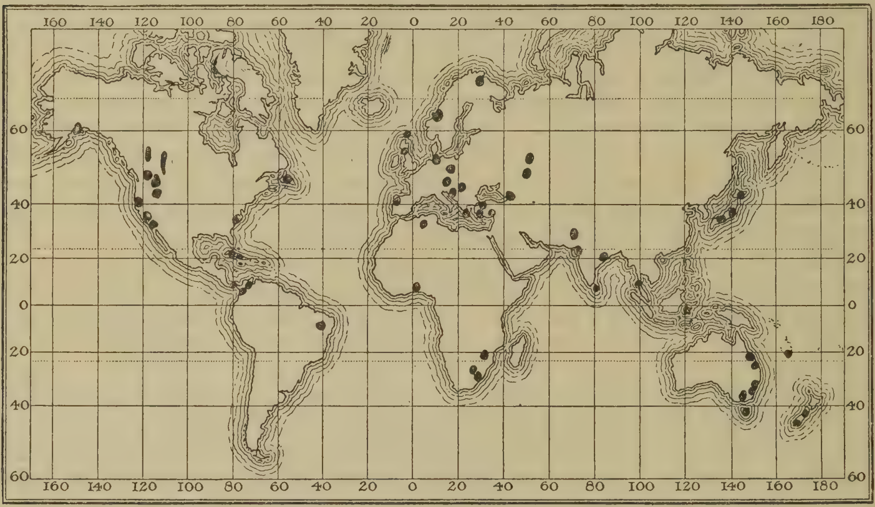


FIG. 1.—Geographical Distribution of Chrome Ores.

Asia.—In Northern **Borneo**, there are deposits on the Malliwalli Island, and chromite sands on the Marasinsing Beach. In the Islands of **Celebes,**[23] also, there are chromite sands. In **Ceylon**, alluvial chromite occurs in the Bambarabotuwa district. In **India,**[24] chromite occurs in the periodotite rocks near Salem, Madras, and also in the Andaman. There is a deposit near Khanogia, Pischin, and in the districts of Mysore, Hassan, and Shimoga of the State of Mysore. There are also deposits of chromite in Bihar and Orissa of the Singhbhum district near Retnagiri, Bombay Presidency; and in the Hindubagh district of Baluchistan. In **Asia Minor,**[25] deposits were discovered in 1848; and from about 1860 to 1903, that country supplied about half the world's output. There are several mines near Brusa. There are also deposits in Smyrna, Adana, Konia, and Anatolia. In the **Netherlands East Indies,** there is a deposit to the north of Malili, Celebes. In **Japan,**[26] there are deposits at Wakamatsu, Province of Hoki, and at Mukawa, Province of Iburi.

Africa.—In **Rhodesia,**[27] the deposits near Selukwe, Southern Rhodesia, have for some years yielded a larger output than any others. There are also deposits in Lomagundi, Victoria, and Makwiro. In **Natal**, chromite occurs at Tugela Rand, near Krantz Kop. In the **Transvaal,**[28] chromite occurs west of Pretoria; and in the districts of Lydenburg, and Rustenberg. In **Togoland,**[29] West Africa, there is a deposit between Lome and Atakpame. It also occurs in **Algeria.**

America.—In **Alaska,**[30] there are deposits of chromite on the Red Mountain, Kenai peninsula. In **Canada**,[31] chromite occurs in the neighbourhood of Coleraive, Thetford and Black Lake in the Province of Quebec. The Mastadon claim, British Columbia,[32] produced about 800 tons of chromite in 1918. There are deposits at Port au Hay, at Benoit Brook, and near the Bay d'Est river, Newfoundland. Many deposits of chromite occur in the **United States.** It occurs in thirty-two counties of the State of California: [33] Alameda, Amador, Butte, Calaveras, Colusa, Del Norte, El Dorado, Fresno, Glenn, Humboldt, Lape, Mariposa, Mendocino, Monterey, Napa, Nevada, Placer, Plumas, San Benito, San Luis Obispo, Santa Barbara, Santa Clara, Shasta, Sierra, Suskiyow, Sonoma, Stanislaus, Tehama, Trinity, Tulare, and Tuolumine; near Big Timber, and Boulder River, in Montana; at Mine Hill, and near Big Ivey Creek,[34] North Carolina; at Golconda, Oregon; [35] in Maryland; [36] in Wyoming; and on the Pacific Coast.[37] There are also chromite deposits in **Nicaragua**, in the Jalapa County, **Guatemala**; and in several parts of **Cuba.**[38] In **Brazil,**[39] there are deposits north-west of Bahia; and in **Colombia**, at Antioquia.

Australasia.—In **New Caledonia,**[40] important deposits are located amongst the mountains in the southern part of the Island. In **Australia**, there are deposits between Keppel Bay and Marlborough, Queensland; [41] near Nundl, Pueka, and Mount Lighting, New South Wales; Gippsland, Victoria; and North Dundas, and Ironstone Hill, Tasmania; and a chromiferous iron ore occurs at North Coolgardie, West Australia. In **New Zealand,**[42] chromite deposits occur at Onatea, Croiselles Harbour; in the Dun Mountain; Moke Creek, Milford Sound, in Otago; and between D'Urville Island and the gorge of Wairva River.

In 1924, the price of chrome ore ranged from 9*s.* 6*d.* to 11*s.* per unit. The world's production of chromite ore in 1913 and 1916, expressed in long tons of 2240 lb. avoir., was respectively, India, 5676, and 20,159; New Caledonia, 62,351, and 72,924; South Rhodesia, 56,593, and 79,349; Canada, —, and 24,568; Australia, 677, and 451; Bosnia, 300, and —; Greece, 6240, and 972; Japan, 1289, and 8147; and the United States, 255, and 47,034. The World's productions in these years were respectively 133,381 and 262,353. For 1922, the results were:

United Kingdom	595	Russia	1,500
South Rhodesia	83,460	Cuba	1
Union South Africa	86	Guatemala	—
Canada	685	United States	420
India	22,777	Brazil	—
Australia	529	Asia Minor	2,500
Greece	9,768	Japan	3,696
Jugoslavia	16	New Caledonia	19,063
Rumania	30	World	145,000

The minerals containing chromates include natural lead chromate, **crocoite,** or **crocoisite,** $PbCrO_4$; **phoenicochroite,** or **melanochroite,** or **phoenicite,** $3PbO.2CrO_3$; **beresowite** or **beresovite,** $6PbO.3CrO_3.CO_2$; **vauquelinite,** and **laxmannite,** $2(Pb,Cu)CrO_4.(Pb,Cu)_3(PO_4)_2$; **tarapacaite,** K_2CrO_4, mixed with sodium and potassium salts; **jossaite** contains chromates of lead and zinc; **dietzeite,** an iodate and chromate of calcium. These are also **daubreeite,** $FeCr_2S_4$; **redingtonite,** a hydrated chromic sulphate; **chromite,** $FeO.Cr_2O_3$; **magnochromite,** $(Mg,Fe)O.Cr_2O_3$; and **chromitite,** $(Fe,Al)_2O_3.2Cr_2O_3$.

C. Porlezza and A. Donati [43] observed the presence of chromium in the volcanic tufa of Fiuggi; and A. Donati, in the products of the Stromboli eruption of 1916. There is a number of silicate minerals containing chromium; in some cases the chromium is regarded as an essential constituent; in others, as a tinctorial agent—R. Klemm. The chromosilicates have been previously discussed—**6.** 40, 865. There are the calcium chrome garnet, *uwarowite;* the hydrated chromium aluminium iron silicate, *wolchonskoite;* the bright green, clayey *chrome ochre—selwynite, milochite, alexandrolite, cosmochlore* or *cosmochromite;* the chrome-augite, *omphacite* or *omphazite;* the augitic *diaclasite;* the *chromediopside;* *chromdiallage;* the *chrome-epidote* of F. Zambonini [44] or the *tawmawite* of A. W. G. Blaeck; the chromic mica *fuchsite;* the chromic muscovite, *avalite;* the chromic chlorite *kämmererite*—and the variety *rhodochrome;* as well as *chromochlorite* or *rhodophyllite*, and *pennine;* the chromic clinochlor, *ripidolite*, and *kotschubeyite;* *serpentine;* and *chromotourmaline.*

P. Groth,[45] G. Rose, and A. Schrauf found chromium in *wulfenite.* The coloration of minerals by chromium was discussed by W. Hermann,[46] K. Schlossmacher, and A. Verneuil. The coloured alumina *smaragd, sapphire,* and *syenite* are chromiferous. Some spinels are chromiferous—*e.g. chromospinel ;* and the so-called *picotite,* or *chromopicotite,* is a chromospinel ; while *alexandrite* is a chromiferous beryl. K. A. Redlich [47] described a chromiferous *talc ;* and K. Zimanyi, a chromiferous *aluminium phosphate.* Chromium occurs in the phosphate rocks of Idaho and Utah. B. Hasselberg reported traces of chromium in a specimen of *rutile* he examined spectroscopically ; E. Harbich, in *amphibole ;* and H. O'Daniel, in *pyroxene ;* A. Jorissen found chromium in the *coal* of La Haye, and the flue-dust from this fuel had 0·04 per cent. of Cr. H. Weger reported chromium in a sample of *graphite ;* F. Zambonini found chromium spectroscopically in vesbine of the crevices, etc., and in the Vesuvian lava of 1631. R. Hermann, A. Vogel, C. E. Claus, P. Collier, and G. C. Hoffmann observed chromium associated with native *platinum ;* and J. E. Stead, with *iron,* and *steel,* and basic and other slags.

Compounds of chromium do not play any known part in the economy of animals or plants ; and it has rarely been detected in animal or vegetable products. E. Demarçay [48] observed, spectroscopically, traces of chromium in the ash of Scotch fir, silver fir, vine, oak, poplar, and horn-beam ; and L. Gouldin found it in the fruit of a rose.

References.

[1] J. G. Lehmann, *De nova mineral plumbi speciae crystallina rubra,* Petropoli, 1766 ; *Nov. Comm. Acad. Petrop.,* **12**. 356, 1766 ; P. S. Pallas, *Reise durch verschiedene Provinzen des russischen Reichs,* St. Petersburg, **2**. 235, 1771 ; J. G. Wallerius, *Systema mineralogicum,* Wein, 1778 ; A. G. Werner, *Von den äusserlichen Kennzeichen der Fossilien,* Leipzig, 296, 1774 ; L. C. H. Macquart, *Journ. Phys.,* **34**. 389, 1789 ; L. N. Vauquelin, *ib.,* **45**. 393, 1794 ; **46**. 152, 311, 1798 ; *Journ. Mines,* **6**. 737, 1797 ; *Nicholson's Journ.,* **2**. 387, 441, 1799 ; *Phil. Mag.,* **1**. 279, 361, 1798 ; **2**. 74, 1798 ; *Ann. Chim. Phys.,* (1), **25**. 21, 194, 1798 ; (1), **70**. 70, 1809 ; S. M. Godon de St. Menin, *ib.,* (1), **53**. 222, 1805 ; *Ann. Musee Hist. Nat.,* **4**. 238, 1804 ; *Phil. Mag.,* **20**. 266, 1805 ; M. H. Klaproth, *Crell's Ann.,* 1, 80, 1798 ; *Ann. Chim. Phys.,* (1), **25**. 273, 337, 1798 ; *Journ. Mines,* **7**. 145, 1798 ; *Nicholson's Journ.,* **2**. 372, 1790 ; *Phil. Mag.,* **1**. 78, 1798 ; J. J. Bindheim, *Schrift. Ges. Nat. Berlin,* **8**. 354, 1788 ; **9**. 101, 1789 ; J. F. Gmelin, *Comment. Gött.,* **14**. 20, 1799 ; A. Mussin-Puschkin, *Crell's Ann.,* i, 355, 1798 ; ii, 444, 1798 ; J. B. Richter, *Ueber die neueren Gegenstände der Chymie,* Breslau, **10**. 30, 1802 ; *Gehlen's Journ.,* **5**. 351, 1805 ; F. Brandenburg, *Schweigger's Journ.,* **13**. 274, 1815 ; J. W. Döbereiner, *ib.,* **22**. 476, 1818 ; K. F. W. Meissner, *Gilbert's Ann.,* **60**. 366, 1818.

[2] F. W. Clarke, *The Data of Geochemistry,* Washington, 34, 1924 ; F. W. Clarke and H. S. Washington, *Proc. Nat. Acad.,* **8**. 112, 1922 ; *The Composition of the Earth's Crust,* Washington, 20, 1924 ; J. H. L. Vogt, *Zeit. prakt. Geol.,* **6**. 226, 315, 377, 413, 1898 ; **7**. 10, 274, 1899 ; **14**. 223, 1906 ; V. Vernadsky, *Essai de minéralogie descriptive,* St. Petersburg, **1**. 121, 740, 1914 ; *La geochimie,* Paris, 16, 1924 ; A. E. Fersman, *Bull. Acad. St. Petersburg,* (6), **6**. 367, 1912 ; H. S. Washington, *Trans. Amer. Inst. Min. Eng.,* **39**. 735, 1908 ; *Bull. Nat. Research Council,* **2**. ii, 30, 1926 ; *Journ. Franklin Inst.,* **190**. 777, 1920 ; *Amer. Journ. Science,* (4), **38**. 90, 1914 ; (5), **9**. 351, 1925 ; (5), **12**. 272, 1926 ; *Journ. Washington Acad.,* **14**. 435, 1924 ; V. M. Goldschmidt, *Videnskapsselskapets Schrift.,* 11, 1922 ; 3, 1923 ; *Zeit. Elektrochem.,* **28**. 411, 1922 ; *Der Stoffwechsel der Erde,* Kristiania, 1922 ; G. Tammann, *Zeit. anorg. Chem.,* **131**. 96, 1923 ; **134**. 269, 1924 ; E. Herlinger, *Forschr. Min.,* **12**. 253, 1927 ; A. von Antropoff, *Sitzber. Nat. Hist. Ver. Rheinlande,* 1, 1926 ; O. Hahn, *Naturwiss.,* **14**, 159, 1926 ; W. and J. Noddack and O. Berg, *ib.,* **13**. 568, 1925 ; J. Joly, *The Surface History of the Earth,* Oxford, 1926 ; P. Pondal, *Anal. Fis. Quim.,* **28**. 488, 1930 ; P. Niggli, *Die leichtflüchtigen Bestandteile im Magma,* Leipzig, 5, 1920 ; *Geochemie und Konstitution der Atomkerne,* Helsingfors, 50, 1928 ; *Naturwiss.,* **9**. 463, 1921 ; G. Berg, *Vorkommen und Geochemie der mineralischen Rohstoffe,* Leipzig, 1929 ; R. A. Sonder, *Zeit. Kryst.,* **57**. 611, 1923 ; *Zeit. anorg. Chem.,* **192**. 257, 1930.

[3] L. W. Gilbert, *Gilbert's Ann.,* **31**. 305, 1809 ; F. Stromeyer, *ib.,* **42**. 105, 1812 ; A. Laugier, *Ann. Museum Hist. Nat.,* **7**. 392, 1806 ; *Journ. Phys.,* **90**. 312, 1820 ; **94**. 156, 1822 ; *Ann. Chim. Phys.,* (2), **19**. 264, 1821 ; *Quart. Journ. Science,* **10**. 189, 1821 ; **13**. 419, 438, 1821 ; C. F. Rammelsberg, *Chemische Natur der Meteoriten,* Berlin, **1**. 98, 1870 ; *Sitzber. Akad. Berlin,* 244, 1844 ; 75, 324, 1870 ; *Pogg. Ann.,* **42**. 458, 1844 ; E. H. von Baumhauer and F. Seelheim, *ib.,* **116**. 187, 1862 ; E. H. von Baumhauer, *ib.,* **66**. 494, 1845 ; J. J. Berzelius, *ib.,* **33**. 1, 1834 ; *Oefvers. Acad. Förhl.,* 115, 1834 ; C. W. Shepard, *Amer. Journ. Science,* (2), **2**. 382, 1846 ; (2), **15**. 365, 1853 ; J. L. Smith, *ib.,* (2), **40**. 215, 1865 ; (3), **21**. 461, 1881 ; *Compt. Rend.,* **92**. 991, 1881 ; G. Chancel and A. Mortessier, *ib.,* **48**. 481, 1859 ; F. Pisani, *ib.,* **62**. 1326, 1866 ; A. Damour,

ib., **55**. 593, 1862 ; C. L. Vlaanderen, *ib.*, **75**. 1678, 1872 ; S. Meunier, *ib.*, **66**. 639, 1868 ; A. Daubrée, *ib.*, **62**. 77, 1866 ; **91**. 30, 1880 ; G. F. Kunz, *Amer. Journ. Science*, (3), **34**. 477, 1887 ; E. S. Dana and S. L. Penfield, *ib.*, (3), **32**. 228, 1886 ; J. F. John, *Chemische Untersuchungen*, Berlin, **6**. 284, 1821 ; *Ann. Chim. Phys.*, (2), **18**. 198, 1821 ; W. Tassin, *Proc. U.S. Nat. Museum*, **34**. 685, 1909 ; O. W. Huntington, *Proc. Amer. Acad.*, **26**. 6, 1891 ; F. Wöhler, *Sitzber. Akad. Wien*, **34**. 11, 1859 ; **46**. 303, 1862 ; G. Tschermak, *ib.*, **61**. 468, 1870 ; **88**. 362, 1883 ; W. Haidinger and C. von Hauer, *ib.*, **41**. 257, 1860 ; G. Rose, *Sitzber. Akad. Berlin*, 80, 88, 115, 123, 139, 1863 ; A. Klein, *Stahl Eisen*, **26**. 396, 1906 ; N. S. Maskelyne, *Phil. Trans.*, **160**. 189, 1870 ; **161**. 359, 1871 ; V. Wartha, *Zeit. anal. Chem.*, **17**. 433, 1878 ; W. Pillitz, *ib.*, **17**. 67, 1878 ; A. Eberhard, *Arch. Naturkunde Dorpat*, **9**. 137, 1882 ; L. Fletcher, *Min. Mag.*, **7**. 183, 1887 ; H. B. von Foullon, *Ann. Hofmuseum Wein*, **3**. 195, 1888 ; E. Cohen, *ib.*, **9**. 118, 1894 ; *Meteoritenkunde*, Stuttgart, **1**. 244, 1894 ; T. Tschernyschoff, *Zeit. deut. geol. Ges.*, **35**. 191, 1883 ; A. Goebel, *ib.*, **1**. 482, 1857 ; A. Kuhlberg, *ib.*, **4**. 10, 1867 ; P. Grigorjeff, *ib.*, **32**. 419, 1880 ; R. D. M. Verbeck, *Jaarb. Nederlandsch Oost-Indie*, **15**, 1886 ; J. W. Retgers, *ib.*, **23**, 1886 ; J. N. Lockyer, *Proc. Roy. Soc.*, **43**. 117, 1887 ; S. M. Losanitsch, *Ber.*, **11**. 98, 1878 ; **25**. 878, 1892 ; P. G. Melekoff, *ib.*, **40**. 367, 1878 ; W. Will and J. Pinnow, *ib.*, **23**. 348, 1890 ; C. Winkler, *Nova Acta Leop. Carol. Akad.*, **40**. 367, 1878 ; G. vom Rath, *Festschrift Niederrh. Ges. Bonn*, 152, 1868 ; E. P. Harris, *Liebig's Ann.*, **110**. 184, 1859 ; J. N. Lockyer, *Proc. Roy. Soc.*, **43**. 117, 1887 ; A. F. G. Werther, *Schrift. Phys. Oekon. Ges. Königsberg*, **8**. 36, 1867 ; A. Koch, *Ber. Math. Naturwiss. Ungarn*, **1**. 346, 1883 ; A. Schwager, *Sitzber. Akad. München*, **8**. 39, 1878 ; J. H. L. Borgström, *Geol. För. Förh. Stockholm*, **33**. 331, 1908 ; P. W. Merrill, *Astrophys. Journ.*, **69**. 330, 1929.

[4] R. Wildt, *Zeit. Physik*, **54**. 856, 1929 ; T. Dunham and C. E. Moore, *Astrophys. Journ.*, **68**. 37, 1928 ; H. A. Rowland, *Preliminary Table of Solar Spectrum Wave-lengths*, Chicago, 1898 ; *Johns Hopkins Univ. Circular*, 85, 1891 ; *Amer. Journ. Science*, (3), **41**. 243, 1891 ; *Chem. News*, **63**. 133, 1891 ; G. Castelli, *Rass. Min. Met. Chim.*, **59**. 1, 1923 ; E. Simpson, *Eng. Min. Journ.*, **121**. 90, 1926 ; H. Deslandres, *Compt. Rend.*, **141**. 409, 1905 ; G. Kirchhoff, *Sitzber. Akad. Berlin*, 63, 1861 ; 227, 1863 ; J. N. Lockyer, *Phil. Trans.*, **172**. 561, 1881 ; J. N. Lockyer and F. E. Baxendall, *Proc. Roy. Soc.*, **74**. 255, 1904 ; F. C. Baxendall, *Researches on the Chemical Origin of Various Lines in Solar and Stellar Spectra*, London, 1910 ; F. McClean, *Monthly Notices Roy. Astron. Soc.*, **52**. 22, 1891 ; H. Deslandres, *Compt. Rend.*, **188**. 669, 1929 ; P. W. Merrill, *Astrophys. Journ.*, **69**. 330, 1929 ; S. A. Mitchell, *ib.*, **71**. 1, 1930.

[5] J. T. Singewald, *Econ. Geol.*, **34**. 645, 1929 ; C. S. Ross, *ib.*, **34**. 641, 1929 ; E. Sampson, *ib.*, **34**. 632, 1929 ; M. E. Glasser, *Ann. Mines*, (10), **5**. 69, 1904 ; E. A. V. Zeally, *Trans. Geol. Soc. South Africa*, **17**. 60, 1914 ; P. A. Wagner, *South African Journ. Science*, **20**. 223, 1923 ; F. Ryba, *Zeit. prakt. Geol.*, **8**. 337, 1900 ; J. H. L. Vogt, *ib.*, **2**. 384, 1894 ; C. S. Hitchin, *Mining Mag.*, **40**. 18, 1929 ; J. S. Diller, *Bull. U.S. Geol. Sur.*, 725, 1921 ; A. C. Gill, *ib.*, 742, 1922 ; W. N. Benson, *Amer. Journ. Science*, (4), **46**. 693, 1918 ; L. W. Fisher, *Econ. Geol.*, **24**. 691, 1929.

[6] W. G. Rumbold, *Chromium Ore*, London, 1921 ; S. P. de Rubies, *Anal. Fis. Quim.*, **15**. 61, 1917 ; Williams, *Chem. News*, **117**. 348, 1918 ; M. E. Wadsworth, *Lithological Studies*, Cambridge, Mass., 1884 ; *Mem. Mus. Compt. Zuol.*, **11**. 1, 1884 ; S. H. Dolbear, *Min. Scient. Press*, **114**. 552, 1917 ; H. Ries, *Eng. Min. Journ.*, **104**. 988, 1917 ; J. S. Diller, *Trans. Amer. Inst. Min. Met. Eng.*, **63**. 105, 1919 ; J. Clouet, *Compt. Rend.*, **67**. 762, 1868 ; *Ann. Chim. Phys.*, (4), **16**. 90, 1849 ; W. Venetor and E. Etienne, *Chem. Ztg.*, **11**. 53, 1887.

[7] A. Strahan, J. S. Flett, and C. H. Dinham, *Chromite, Special Reports on the Mineral Resources of Great Britain*, London, 5. 29, 1916 ; A. Russell, *Min. Mag.*, **18**. 14, 1918 ; C. S. Hitchin, *Mining Mag.*, **40**. 18, 1929.

[8] F. Ryba, *Zeit. prakt. Geol.*, **8**. 337, 1900 ; R. Helmhecker, *Mineral Ind.*, **4**. 94, 1895.

[9] W. Soltz, *Oesterr. Zeit. Berg. Hütt.*, **51**. 19, 1893 ; R. Helmhacker, *Mineral Ind.*, **4**. 94, 1896.

[10] C. von John, *Jahrb. geol. Reichsanst.*, **53**. 502, 1904.

[11] H. Traube, *Zeit. deut. geol. Ges.*, **46**. 50, 1894 ; B. Kosmann, *ib.*, **42**. 794, 1890 ; **44**. 359, 1892 ; A. Knop, *Neues Jahrb. Min.*, 697, 1877 ; D. Leo, *Stahl Eisen*, **11**. 643, 1891.

[12] A. Stella, *Rass. Min.*, **63**. 32, 1925 ; P. Lepez, *Metall Erz*, **26**. 85, 1929.

[13] H. K. Scott, *Journ. Iron Steel Inst.*, **87**. i, 447, 1913 ; A. Christomanos, *Ber.*, **10**. 343, 1877 ; E. McDonell, *Board Trade Journ.*, **57**. 377, 1907.

[14] E. Nowack, *Montan. Rund.*, **16**. 695, 1924 ; D. A. Wray, *Mining Mag.*, **32**. 329, 1925.

[15] L. Dominian, *Eng. Min. Journ.*, **78**. 185, 1905.

[16] J. H. L. Vogt, *Zeit. prakt. Geol.*, **2**. 381, 1894.

[17] F. R. Tegengren, *Teknisk Tids.*, **43**. 26, 1913.

[18] F. W. Foote and R. S. Ranson, *Eng. Min. Journ.*, **106**. 51, 1918.

[19] P. Pilz, *Zeit. prakt. Geol.*, **22**. 373, 1914.

[20] W. Venator and E. Etienne, *Chem. Ztg.*, **11**. 53, 1886 ; A. Arzruni, *Zeit. Kryst.*, **8**. 330, 1884 ; A. Moberg, *Journ. prakt. Chem.*, (1), **43**. 119, 1848 ; N. Besborodko, *Neues Jahrb. Min. B.B.*, **34**. 783, 1912 ; A. Vogel, *Repert. Pharm.*, **22**. 392, 1873 ; L. Duparc and S. P. de Rubies, *Anal. Fis. Quim.*, **11**. 367, 1913.

[21] M. Z. Jovitschitsch, *Bull. Soc. Min.*, **35**. 511, 1913 ; B. Baumgästel, *Tschermak's Mitt.*, (2), **23**. 393, 1904.

[22] P. Lepez, *Metall Erz*, **25**. 299, 1928 ; E. Nowack, *Montan. Rund.*, **16**. 965, 1924 ; D. A. Wray, *Mining Mag.*, **32**. 329, 1925.

[23] Anon., *Iron Coal Trades Rev.*, **97**. 454, 1918.

[24] W. F. Smeeth and P. S. Iyengar, *Bull. Mysore Dept. Mines*, 7, 1916 ; C. Mahadevan, *Econ. Geol.*, **24**. 195, 1929 ; A. L. Coulson, *Rec. Geol. Sur. India*, **62**. 185, 1929 ; E. Vredenburg, *Gen. Rep. Geol. Sur. India*, 9, 1903 ; E. Krenkel, *Zeit. prakt. Geol.*, **38**. 81, 1930.

[25] N. M. Penzer, *Mining Mag.*, **21**. 218, 1919 ; F. Fuech, *Glückauf*, **51**. 381, 412, 438, 464, 1915 ; G. B. Ravndal, *Dept. U.S. Commerce*, 292, 1919 ; K. E. Weiss, *Zeit. prakt. Geol.*, **9**. 250, 1901 ; Anon., *Eng. Min. Journ.*, **128**. 83, 103, 1920 ; E. L. Harris, *ib.*, **85**. 1088, 1908 ; W. F. Wilkinson, *Journ. Geol. Soc.*, **51**. 95, 1895 ; W. F. A. Thomas, *Trans. Amer. Inst. Min. Eng.*, **28**. 208, 1899.

[26] E. Divers, *Chem. News*, **44**. 217, 1881 ; T. Kato, *Journ. Japan Geol. Soc.*, **28**. 1, 1921.

[27] K. E. V. Zealley, *Mining Mag.*, **12**. 108, 1915 ; *Trans. Geol. Soc. South Africa*, **17**. 60, 1914 ; *Bull. S. Rhodesia Geol. Sur.*, 3, 1919 ; F. P. Mennell, *S. African Journ. Ind.*, **1**. 1302, 1411, 1918 ; *S. African Journ. Science*, **20**. 223, 1923 ; A. Stutzer, *Metall Erz*, **17**. 249, 1920 ; F. E. Kap, *Rep. South Rhodesia Geol. Sur.*, 223, 1928.

[28] A. L. Hall and W. A. Humphrey, *Trans. Geol. Soc. South Africa*, **11**. 69, 1908 ; Anon., *S. African Eng. Min. Journ.*, 539, 1925 ; R. Stappenbeck, *Metall Erz*, **27**. 381, 1930 ; C. A. C. Tremier, *Board Trade Journ.*, **57**. 377, 1907.

[29] M. Koert, *Amstsblatt Schutzgebiet Togo*, 13, 1908 ; H. Arsandaux, *Bull. Soc. Min.*, **48**. 70, 1925 ; *Geo. Centr.*, **11**. 707, 1908.

[30] A. C. Gill, *Bull. U.S. Geol. Sur.*, 712, 1919 ; 742, 1922 ; G. C. Martin, *ib.*, 692, 1919.

[31] M. Penhale, *Min. Ind.*, 92, 1895 ; F. Cirkel, *Report on the Chrome Iron Ore Deposits in the Eastern Townships, Province of Quebec*, Ottawa, 1909 ; L. Reinecke, *Mem. Canada Geol. Sur.*, 118, 1920 ; G. A. Young, *Bull. Canada Geol. Sur.*, 1085, 1909 ; R. Harvie, *Rev. Min. Oper. Quebec*, 148, 1914 ; J. A. Dresser, *Canadian Min. Journ.*, **30**. 365, 1909 ; F. Cirkel, *Canada Dept. Mines, Journ. Canadian Min. Inst.*, **22**. 871, 940, 1030, 1919 ; W. H. Edwards, *ib.*, **9**. 35, 1906 ; J. G. Ross, *ib.*, **22**. 1204, 1919 ; J. T. Donald, *ib.*, **12**. 25, 1899 ; *Canada Mining Rev.*, **13**. 204, 1895 ; *Journ. Min. Assoc. Quebec*, 108, 1895 ; J. Obalsky, *ib.*, 11, 1895 ; *Canada Mining Rev.*, **13**. 205, 1895 ; H. F. Strangeways, *Trans. Canada Soc. Civil Eng.*, **21**. 232, 1908.

[32] W. M. Brewer, *Rept. Minister Interior B.C.*, 285, 1915.

[33] S. H. Dolbear, *Stahl Eisen*, **34**. 1694, 1914 ; *Min. Scient. Press*, **110**. 356, 1915 ; W. M. Bradley, *Bull. Cal. Min. Bur.*, 76, 1918 ; J. S. Diller, *Trans. Amer. Inst. Min. Eng.*, **63**. 105, 1920 ; *Bull. U.S. Geol. Sur.*, 725, 1921 ; E. C. Harder, *Mining World*, **33**. 611, 1910 ; H. Pemberton, *Chem. News*, **63**. 241, 1891 ; *Journ. Franklin Inst.*, **131**. 387, 1891 ; J. H. Pratt, *Trans. Amer. Inst. Min. Eng.*, **29**. 17, 1900 ; *Ann. New York Acad.*, **11**. 489, 1899 ; *Eng. Min. Journ.*, **70**. 190, 1900.

[34] J. H. Pratt, *Amer. Journ. Science*, (4), **7**. 281, 1899 ; *Trans. Amer. Inst. Min. Eng.*, **29**. 17, 1899 ; J. H. Pratt and J. V. Lewis, *Bull. North Carolina Geol. Sur.*, **1**. 369, 1905 ; *Eng. Min. Journ.*, **109**. 1112, 1920.

[35] J. S. Diller, *Bull. U.S. Geol. Sur.*, 548, 1914.

[36] W. Glenn, *Trans. Amer. Inst. Min. Eng.*, **25**. 481, 1896 ; J. T. Singewald, *Econ. Geol.*, **14**. 189, 1919.

[37] J. F. Grugan, *Chem. Met. Engg.*, **20**. 79, 1919.

[38] J. S. Cox, *Trans. Amer. Inst. Min. Eng.*, **43**. 73, 1911 ; E. F. Burchard, *ib.*, **63**. 150, 1919 ; E. S. Murias, *Eng. Min. Journ.*, **114**. 197, 1922 ; E. F. Burchard, *Trans. Amer. Inst. Min. Eng.*, **63**. 208, 1920 ; Anon., *Iron Trades Rev.*, **63**. 1238, 1918.

[39] H. E. Williams, *Eng. Min. Journ.*, **111**. 376, 1921.

[40] R. H. Compton, *Geol. Journ.*, **49**. 81, 1917 ; A. Liversidge, *Journ. Roy. Soc. New South Wales*, **14**. 227, 1881 ; E. Glasser, *Ann. Mines*, (10), **4**. 299, 1903 ; (10), **5**. 29, 69, 503, 1904 ; C. Dufay, *Compt. Rend. Soc. Ind. Min.*, 220, 1906 ; F. D. Power, *Trans. Inst. Min. Met.*, **8**. 426, 1900 ; Anon., *Rev. Minera*, **42**. 183, 1891 ; J. Garnier, *Mém. Soc. Ing. Civils*, 244, 1887.

[41] B. Dunstan, *Queensland Govt. Min. Journ.*, **17**. 421, 1916 ; E. C. S. Smith, *ib.*, **19**. 57, 1919 ; W. N. Benson, *Proc. Linn. Soc. New South Wales*, **38**. 569, 662, 1913 ; H. G. Raggatl, *Bull. N.S.W. Geol. Sur.*, 13, 1925 ; E. Govett, *Min. Ind.*, **3**. 122, 1895 ; J. E. Carne, *Eng. Min. Journ.*, **59**. 603, 1895 ; *Min. Resources N.S.W.*, 1, 1898.

[42] H. M. Johnstone, *Geology of Tasmania*, Hobart, 1888 ; P. H. Morgan and J. Henderson, *N.Z. Journ. Science Tech.*, **2**. 43, 1919 ; R. W. E. MacIvor, *Chem. News*, **57**. 1, 1888 ; J. Plummer, *Eng. Min. Journ.*, **59**. 508, 1895 ; A. M'Kay, *ib.*, **65**. 190, 1898.

[43] C. Porlezza and A. Donati, *Ann. Chim. Applicata*, **16**. 457, 1926 ; A. Donati, *ib.*, **16**. 475, 1926 ; R. Klemm, *Centr. Min.*, 267, 1927.

[44] F. Zambonini, *Boll. Com. Geol. Ital.*, **47**. 80, 1920 ; A. W. G. Blaeck, *Rec. Geol. Sur. India*, **36**. 254, 1908.

[45] P. Groth, *Zeit. Kryst.*, **7**. 592, 1883 ; G. Rose, *Reise nach dem Ural, dem Altai, und dem Kaspischen Meere*, Berlin, **2**. 10, 1842 ; *Pogg. Ann.*, **46**. 639, 1839 ; A. Schrauf, *Sitzber. Akad. Wien*, **63**. 184, 1871 ; *Proc. Roy. Soc.*, **19**. 451, 1871.

[46] W. Hermann, *Zeit. anorg. Chem.*, **60**. 369, 1908 ; A. Verneuil, *Compt. Rend.*, **151**. 1063, 1910 ; K. Schlossmacher, *Zeit. Kryst.*, **75**. 399, 1930.

[47] B. Hasselberg, *Bihung Kisvenska Akad.*, **23**. 3, 1897 ; A. Jorissen, *Bull. Acad. Belg.*, 178, 1905 ; H. Weger, *Der Graphit*, Berlin, 11, 1872 ; W. Lindgren, *Econ. Geol.*, **18**. 441, 1923 ; A. Vogel, *Repert. Pharm.*, **22**. 392, 1873 ; R. Hermann, *Journ. prakt. Chem.*, (1), **23**. 276, 1841 ; C. E. Claus, *ib.*, (1), **80**. 285, 1860 ; F. Zambonini, *Amer. Min.*, **12**. 1, 1927 ; P. Collier, *Amer. Journ. Science*, (3), **21**. 123, 1881 ; G. C. Hoffmann, *Trans. Roy. Soc. Canada*, (3), **5**. 17, 1887 ;

K. A. Redlich, *Zeit. prakt. Geol.*, **19**. 126, 1911; K. Zimanyi, *Ber. Math. Naturwiss. Ungarn.*, **25**. 241, 1910; H. O. Daniel, *Zeit. Kryst.*, **75**. 575, 1930; E. Harbich, *Tschermak's Mitt.*, (2), **40**. 191, 1929; J. E. Stead, *Journ. Iron Steel Inst.*, **43**. i, 153, 1893.

[48] E. Demarçay, *Compt. Rend.*, **130**. 91, 1900; L. Gouldin, *Chem. News*, **100**. 130, 1909.

§ 2. The Extraction of Chromium as Chromic Oxide or Chromate

When the chromite is disseminated in disconnected patches, it is mined by open quarries generally in terraces or benches; and when large, well-defined deposits occur, as at Selukwe, Rhodesia, underground workings are practicable. Chromite is not so hard as quartz, but it is tougher, and does not break so easily. The mining is therefore assisted by blasting. Hand concentration by sorting may be used. Here the ore is separated from waste by means of a hammer; the larger pieces of ore may be broken into coarse lumps in a jaw crusher, and passed on to a revolving table or endless belt for hand-sorting. For concentrating by gravity machines, the ore is crushed moderately fine in a drop-stamping machine or in a ball mill, and then passed by water over a table concentrator whereby it is separated into (i) concentrate—consisting of chromite only; (ii) middling—containing much chromite; (iii) tailings—containing but little chromite and is sent to waste-dump; and (iv) slimes—often containing much chromite in a fine state of subdivision but not usually sufficient to deal with profitably. The middling is re-treated usually on another concentrating table. The tailings and slimes represent loss. The concentrate varies in quality, but it usually exceeds 50 per cent. chromite.[1]

Chromite can be converted into chromic oxide or chromate, by

1. *Dry processes.*—Here the powdered mineral is mixed with an alkali, and something to keep the mass open and porous while it is roasted by an oxidizing flame, say, in a reverberatory furnace, so as to form alkali chromate: $2(FeO.Cr_2O_3)+4Na_2CO_3+7O=Fe_2O_3+4Na_2CrO_4+4CO_2$. This is extracted with water and converted into dichromate by treatment with acid; the dichromate is then reduced to insoluble chromic oxide and a soluble alkali salt which is removed by lixiviation with water. The reaction was studied by A. J. Sofianopoulos, and H. A. Doerner. Technical details are indicated in the usual handbooks.[2]

If calcium chromate be treated with a soln. of potassium sulphate, the calcium chromate is converted into calcium sulphate, which is precipitated, and potassium chromate, which remains in soln. Instead of leaching the calcium chromate with a soln. of potassium sulphate, W. J. Chrystal showed that if ammonium sulphate is used, a soln. of ammonium chromate is produced, and J. J. Hood found that if the soln. of potassium salt be treated with sodium hydrosulphate, potassium sulphate crystallizes from the soln., while sodium dichromate remains in soln. According to F. M. and D. D. Spence and co-workers, if a mixture of ammonia and carbon dioxide be passed into the aq. extract of the calcium chromate, calcium carbonate is precipitated while ammonium and alkali chromate remain in soln. If the liquid be boiled, ammonia is given off, and sodium dichromate remains in soln. S. Pontius used water and carbon dioxide under press. for the leaching process. J. Brock and W. A. Rowell purified alkali chromite by treating the soln. with strontium hydroxide, and digesting the washed precipitate with a soln. of alkali sulphate or carbonate; W. J. A. Donald used calcium hydroxide or barium chloride as precipitant. A mixture of chromite with calcium carbonate and potassium carbonate was formerly much employed. Modifications of the process were described by W. J. A. Donald,[3] A. R. Lindblad, C. J. Head, S. G. Thomas, W. Gow, J. Stevenson and T. Carlile, L. I. Popoff, G. Bessa, P. Weise, P. N. Lukianoff, B. Bogitch, E. Baumgartner, W. Carpmael, Grasselli Chemical Co., N. F. Yushkevich, A. J. Sofianopoulos, R. W. Stimson, H. Specketer and G. Henschel, and C. S. Gorman. J. Booth, and S. G. Thomas heated the chromite to a high temp. before it was treated with the lime-alkali mixture. With the idea of lowering the temp. at which the chromate is formed, F. O. Ward recommended adding calcium fluoride to the mixture; and J. Massignon and E. Vatel added calcium chloride. V. A. Jacquelain recommended calcining a mixture of calcium carbonate and chromite; extracting the calcium chromate with hot water; acidifying the soln. with sulphuric acid; and precipitating the iron by the addition of a little calcium carbonate. The soln. of calcium dichromate can be treated with alkali for the alkali salt. P. Römer used alkali carbonate without the calcium carbonate; the Chemische Fabrik Billwärder digested the chromite with sodium hydroxide in an iron vessel at 500°–600° through which was passed a current of air, an oxidizing agent was also added to the mixture. H. Moissan treated ferro-chromium with fused potassium hydroxide. The Chemische Fabrik Griesheim-Elektron used a modification of the process. G. Wachtel studied the effect of the lime. He said that with lime alone there is a 90 per cent. conversion of chromic oxide used and a 30 per cent. conversion with chromite; and that about 10 per cent. of the chromic oxide acquires the property of dissolving in acids. The yield with potassium carbonate alone is only half as large as when the potassium carbonate is mixed with an equal quantity of lime. Hence, the simultaneous action of the calcium and potassium carbonate on the ore gives better results than when either is used alone. N. F. Yushkevich observed that the formation of chromate with the chromite-lime-sodium carbonate mixture is slow at 700°; at 1160°, 95 per cent. of the chromium is oxidized in thirty minutes; and at 1260° decomposition sets in. L. I. Popoff found that the speed of oxidation of rich ores is quicker than with poor ores, and the percentage yield of chromate is greater. If the chromite contains 30 to 40 per cent. Cr_2O_3, lime to the extent of 80 per cent. of the weight of the ore should be added; 90 per cent. of lime for 40 to 50 per cent. ores; and 120 to 130 per cent. of lime for over 50 per cent. ores. These quantities of lime must be increased if the temp. of oxidation exceeds 1100°. The theoretical quantity of sodium carbonate was used. H. Pincass discussed this subject. P. Römer, and N. Walberg recommended using sodium carbonate in place of the more expensive potassium carbonate. Other alkali salts have been substituted for the carbonate; thus, S. Pontius, R. A. Tilghman, and H. M. Drummond and W. J. A. Donald used alkali sulphate; J. Swindells, sodium chloride; E. P. Potter and W. H. Higgins, sodium sulphate; E. Hene, alkali hydroxide; L. N. Vauquelin, J. B. Trommsdorff, and J. F. W. Nasse, potassium nitrate; and C. S. Gorman heated a mixture of chromite, sodium chloride, and calcium hydroxide in steam at 550°–850°. H. Schwarz found that by using alkali sulphate the potassium chromate can be leached directly from the mass. Instead of using calcium carbonate, C. S. Gorman used magnesium or barium carbonate; F. F. Wolf and L. I. Popoff, iron oxide; H. A. Seegall, barium carbonate; and the Deutsche Solvay-Werke, ferric oxide. P. Monnartz made the ore into briquettes with sand, limestone, and tar; these were fed into a small blast furnace using a blast of air enriched with oxygen. The products were a ferro-chromium alloy, and a slag with 9·4 per cent. chromic oxide. Modifications of the roasting process for chromates were employed by C. Häussermann, F. Filsinger, H. A. Seegall, and J. Uppmann for recovering chromium from chromiferous residues.

W. H. Dyson and L. Aitchison[4] heated chromite mixed with a carbonaceous material to 900° in a mixture of equal vols. of hydrogen chloride and chlorine until all the iron had volatilized; the residue was then heated to 1200° in the same gases to distil off the chromium. W. Crafts reduced the ore with charcoal at 1300° to 1350°, extracted the product with conc. sulphuric acid at 100°; and the chromium may be precipitated by adding calcium chloride to convert the sulphate to chloride and precipitating as hydroxide by limestone; or the chromium can be precipitated electrolytically from the sulphate soln. According to C. Müller and co-workers, chromite is first reduced in hydrogen or in a mixture of gases containing hydrogen and the product is heated above 200° with a slight deficiency of sulphuric acid in a closed vessel lined with hard lead containing preferably 3 per cent. of Sb.

Soln. of chromates can be reduced to chromic salt by hydrogen sulphide (L. N. Vauquelin),[5] sulphur dioxide (A. F. Duflos, and J. B. Trommsdorff), alkali polysulphide (J. J. Berzelius), sulphur in a boiling soln. (G. F. C. Frick, J. L. Lassaigne, and H. Moser)—*vide infra*, chromic oxide.

2. *Wet processes.*—Chromates can be obtained from chromite or chromic oxide in the wet-way. The Chemische Fabrik Griesheim-Elektron [6] digested the powdered mineral with sulphuric acid of sp. gr. about 1·54 with an oxidizing agent like lead or manganese dioxide, potassium permanganate, etc. E. Müller and M. Soller used lead dioxide ; E. Bohlig, potassium permanganate ; E. Donath, manganese dioxide ; P. Waage and H. Kämmerer, bromine ; F. Storck and L. L. de Koninck, chloric acid ; H. Dercum, G. Feyerabend, W. Stein, and M. Balanche, bleaching powder ; and R. von Wagner used a mixture of sodium hydroxide and potassium ferricyanide. The chromium can also be extracted from chromite with acids, etc.

3. *Electrolytic processes.*—R. Lorenz [7] found that a soln. of potassium dichromate can be prepared by passing a current at 2 volts potential between an anode of ferrochrome (containing about equal quantities of chromium and iron) and a cathode of porous copper oxide, the two electrodes dipping in a soln. of potassium hydroxide contained in a beaker. Ferric oxide collects at the bottom of the beaker. The Chemische Fabrik Griesheim-Elektron obtained chromates by electrolytic oxidation with an anode of chromium, or of a chromium alloy—*e.g.* ferrochromium, an iron cathode, and a soln. of an alkali hydroxide separating the anode and cathode by a diaphragm. Sufficient alkali is added to the anode liquid to precipitate the metal alloyed with the chromium of the anode. Chromic acid and ferric sulphate can be separated by fractional crystallization. A modification of the process consists in dissolving the chromium or ferrochromium instead of using it directly as anode and then electrolyzing it, using an insoluble anode, such as lead. The cathode and anode compartments are separated by two diaphragms, and a hydroxide or a carbonate is added to the electrolyte contained in the compartment between the latter. J. Heibling used an alkali chloride or nitrite soln. as anolyte.

C. Häussermann [8] oxidized electrolytically a soln. of chromic hydroxide in soda-lye in the anode compartment, when the cathode liquid was a soln. of an indifferent salt ; D. G. Fitzgerald used an acidic soln. of chromic oxide as anode liquor, and a soln. of a zinc salt about the cathode, and on electrolysis, chromate was formed at the anode and zinc was deposited on the cathode. K. Elbs said that a current efficiency of 70 per cent. can be obtained with freshly-ignited platinum anodes of low current density. F. Regelsberger had no success in the oxidation of chromium salts in acidic soln., even with the use of a diaphragm ; but good results were obtained with alkaline soln., using lead anodes, with or without a diaphragm, with warm soln. M. de Kay Thompson studied the production of chromates by the electrolysis of sodium carbonate or hydroxide soln. with ferrochromium electrodes. E. Müller and M. Soller said that chrome alum dissolved in N-H_2SO_4 is not appreciably oxidized to chromic acid by the use of an anode of smooth platinum ; but a trace of lead in the soln. is precipitated on the anode as lead dioxide, and this brings about oxidation ; traces of chlorine also favour the oxidation. There is about one-third the oxidation with a platinized platinum anode as occurs with a lead dioxide anode. With a lead dioxide anode, the oxidation is almost quantitative in fairly conc. soln. of chrome alum, and a current density of about 0·005 amp. per sq. cm. The difference is not due to the higher potential of the lead dioxide anode, but rather depends on the lead dioxide acting catalytically as a carrier of oxygen. I. Stscherbakoff and O. Essin found that in the electrolytic production of dichromate from chromate a sudden rise in the conductivity of the electrolyte is observed when the composition corresponds to the polychromate, $Na_2Cr_4O_{12}$. In order to obtain the best yields of dichromate, electrolysis may be conducted either in normal chromate soln. at high current density or at lower current density in soln. of the above polychromate composition. According to F. Schmiedt, and A. R. y Miro, the oxidation is favoured by the presence of fluorine ions ; and M. G. Levi and F. Ageno added that with normal soln. of chromium sulphate and N-H_2SO_4, on electrolysis with platinized platinum electrodes in the presence of 0·498N-hydrofluoric acid, the yield of 78 per cent. chromic acid is comparable with that produced by lead dioxide electrodes. The Höchster Farbwerke said that in the electrochemical oxidation of a soln. of chrome alum to chromic acid, it is necessary for conc. sulphuric acid to be present, because, added F. Fichter and E. Brunner, the acid must be conc. enough to furnish sulphur tetroxide. F. Schmiedt found that the oxidation is favoured by the presence of Cy-ions (*e.g.* potassium cyanide or ferrocyanide), many oxidizing agents, compounds of phosphorus and boron, cerous nitrate, sodium molybdate or vanadate, and platinum tetrachloride. The Chemische Fabrik Buckau found that the reduction of chromate by cathodic hydrogen, in cells without diaphragms, is avoided by the use of a little acetic acid or an acetate. The electrolytic oxidation of soln. of chromium salts was also examined by M. le Blanc, F. Regelsberger, F. W. Skirrow, A. R. y Miro, L. Darmstädter, H. R. Carveth and B. E. Curry, and the Farbewerke Meister Lucius and Brüning, A. W. Burwell, I. Stscherbakoff, A. Lottermoser and K. Falk, E. Müller and E. Sauer, R. E. Pearson and E. N. Craig, M. J. Udy, and R. H. McKee and S. T. Leo.

REFERENCES.

[1] K. R. Krishnaswami, *Journ. Indian Inst.*, **10**. 65, 1927.

[2] F. M. and D. D. Spence, and A. Shearer, *Brit. Pat. No.* 5057, 1900; F. M. and D. D. Spence, A. Shearer and T. J. Ireland, *ib.*, 11847, 1900; F. M., D. D. and H. Spence, J. J. Hood and T. J. I. Craig, *ib.*, 5015, 1901; J. J. Hood, *ib.*, 3895, 1885; W. J. Chrystal, *ib.*, 4028, 1884; W. J. A. Donald, *ib.*, 5948, 1884; 6731, 1884; J. Brock and W. A. Rowell, *ib.*, 5260, 1885; H. R. Krishnaswami, *Journ. Indian Inst. Science*, **10**. A, 65, 1927; L. Wickop, *Die Herstellung der Alkalibichromate*, Halle, a.S., 1911; C. Häussermann, *Dingler's Journ.*, **288**. 93, 111, 161, 1893; G. Lunge, *Zeit. angew. Chem.*, **7**. 101, 1894; T. E. Thorpe, *A. Dictionary of Applied Chemistry*, London, **2**. 233, 1921; A. W. Hofmann, *Bericht über die Entwicklung der chemischen Industrie*, Braunschweig, **1**. 723, 1875; F. J. G. Baltzer, *Rev. Gén. Chim.*, **8**. 32, 81, 389, 1905; M. Lewin, *Chem. Ztg.*, **31**. 1076, 1907; H. Fischer, *Die industrielle Herstellung und Verwendung der Chromverbindungen, die dabei entscheiden Gesundheitsgefahren für die Arbeiter und die Massnahmen zu ihrer Bekämpfung*, Berlin, 1911; S. Pontius, *German Pat., D.R.P.* 21589, 1882; A. J. Sofianopoulos, *Journ. Soc. Chem. Ind.*, **49**. T, 279, 1930; B. M. Maletra, *French Pat. No.* 683190, 683602, 1929; H. A. Doerner, *Rep. Investigations U.S. Bur. Mines*, 2999, 1930.

[3] B. Bogitch, *Compt. Rend.*, **178**. 2254, 1924; G. Wachtel, *Journ. Russ. Phys. Chem. Soc.*, **17**. 109, 1885; *Bull. Soc. Chim.*, (2), **45**. 179, 1886; J. Massignon and E. Vatel, *ib.*, (3), **5**. 371, 1891; *Brit. Pat. No.* 2224, 1891; S. G. Thomas, *ib.*, 5130, 1884; W. J. A. Donald, *ib.*, 5086, 1888; W. Carpmael, *ib.*, 226066, 1924; 361647, 1926; C. J. Head, *ib.*, 166289, 1920; H. M. Drummond and W. J. A. Donald, *ib.*, 2594, 1877; E. P. Potter and W. H. Higgins, *ib.*, 587, 1883; 5552, 1884; E. Baumgartner, *ib.*, 197223, 1922; C. S. Gorman, *ib.*, 1781, 2781, 1877; 4195, 4929, 1884; H. A. Seegall, *ib.*, 4602, 1889; R. A. Tilghman, *ib.*, 11555, 1847; J. and J. Stevenson and T. Carlile, *ib.*, 1695, 1873; J. Booth, *U.S. Pat. No.* 95839, 1853; *London Journ. Arts.*, (3), **43**. 432, 1853; J. Swindells, *Brit. Pat. No.* 13342, 1850; L. Wickop, *ib.*, 270143, 1926; P. Römer, *German Pat., D.R.P.* 24694, 1882; 166767, 1904; Deutsche Solvay-Werke, *ib.*, 82980, 1894; Chemische Fabrik Billwärder, *ib.*, 163541, 163814, 1904; 171089, 1905; S. Pontius, *ib.*, 21589, 1882; Chemische Fabrik Griesheim-Elektron, *ib.*, 151132, 1902; G. Bessa, *L'Ind. Chim.*, **9**. 143, 1922; *Chem. Trade Journ.*, **70**. 595, 1922; N. Walberg, *Dingler's Journ.*, **259**. 188, 1886; H. Schwarz, *ib.*, **198**. 159, 1870; A. Gow, *Chem. News*, **39**. 231, 1874; F. O. Ward, *Mech. Mag.*, **4**. 232, 1865; V. A. Jacquelain, *Ann. Chim. Phys.*, (3), **21**. 478, 1847; *Compt. Rend.*, **24**. 439, 1847; P. Monnartz, *Met.*, **6**. 160, 1909; H. Pincass, *Continental Met. Chem. Engg.*, **2**. 233, 1927; L. I. Popoff, *ib.*, **1**. 143, 1927; *Journ. Russ. Chem. Ind.*, **2**. 465, 1926; P. N. Lukianoff, *ib.*, **1**. 11, 1924; C. Häussermann, *Dingler's Journ.*, **288**. 93, 111, 161, 1893; F. Filsinger, *ib.*, **231**. 95, 1879; *Ber.*, **11**. 1138, 1878; J. Uppmann, *Chem. Ind.*, **2**. 55, 1879; *Zeit. Chem. Grossgewerbe*, **3**. 634, 1879; Grasselli Chemical Co., *U.S. Pat. No.* 1526325, 1925; H. Moissan, *Compt. Rend.*, **116**. 349, 1893; **119**. 185, 1894; L. N. Vauquelin, *Journ. Phys.*, **45**. 393, 1794; **46**. 152, 311, 1798; *Journ. Mines.* **6**. 737, 1797; *Nicholson's Journ.*, **2**. 387, 441, 1799; *Phil. Mag.*, **1**. 279, 361, 1798; **2**. 74, 1798; *Ann. Chim. Phys.*, (1), **25**. 21, 194, 1798; (1), **70**. 70, 1809; J. F. W. Nasse, *Schweigger's Journ.*, **43**. 339, 1825; J. B. Trommsdorff, *Trommsdorff's Journ.*, **18**. 225, 1809; N. F. Yushkevich, *Trans. Russ. Inst. Econ. Min.*, **13**, 1925; N. F. Yushkevich and M. N. Levin, *Journ. Russ. Chem. Ind.*, **2**. 329, 1926; N. F. Yushkevich, M. Karzhevin and I. N. Shokin, *Journ. Russ. Chem. Ind.*, **2**. 951, 1926; **3**. 1119, 1926; N. F. Yushkevich and I. N. Shokin, *ib.*, **4**. 204, 1927; F. F. Wolf and L. I. Popoff, *ib.*, **5**. 618, 1928; **6**. 12, 1929; A. R. Lindblad, *Swedish Pat. No.* 51689, 1922; P. Weise, *U.S. Pat. No.* 1631170, 1927; H. Specketer and G. Henschel, *ib.*, 1760788, 1930; E. Hene, *French Pat. No.* 648658,

1928; A. J. Sofianopoulos, *Journ. Soc. Chem. Ind.*, **49**. T, 279, 1930; R. W. Stimson, *Brit. Pat. No.* 320845, 1928.

[4] W. H. Dyson and L. Aitchison, *Brit. Pat. No.* 176729, 1920; 176428, 1921; C. Müller, L. Schlecht, and A. Cure, *German Pat., D.R.P.* 444798, 1924; W. Crafts, *Carnegie Mem. Iron Steel Inst.*, **15**. 175, 1926.

[5] L. N. Vauquelin, *Journ. Phys.*, **45**. 393, 1794; **46**. 152, 311, 1798; *Journ. Mines*, **6**. 737, 1797; *Nicholson's Journ.*, **2**. 387, 441, 1799; *Phil. Mag.*, **1**. 279, 361, 1798; **2**. 74, 1798; *Ann. Chim. Phys.*, (1), **25**. 21, 194, 1798; (1), **70**. 70, 1809; A. F. Duflos, *Brandes' Arch.*, **23**. 166, 1827; J. B. Trommsdorff, *Trommsdorff's Journ.*, **18**. 255, 1809; G. F. C. Frick, *Pogg. Ann.*, **13**. 494, 1823; J. L. Lassaigne, *Ann. Chim. Phys.*, (2), **14**. 299, 1820; H. Moser, *Chemische Abhandlung über das Chrom*, Wien, 1824; *Schweigger's Journ.*, **42**. 99, 1824; J. J. Berzelius, *ib.*, **22**. 53, 1818; *Ann. Chem. Phys.*, (2), **17**. 7, 1821; *Pogg. Ann.*, **1**. 34, 1824.

[6] Chemische Fabrik Griesheim-Elektron, *German Pat., D.R.P.* 143251, 1902; M. Soller, *Die Rolle des Bleisuperoxyde als Anode, besonders bei der elektrolytischen Regeneration der Chromsaure*, Halle a. S., 1905; E. Müller and M. Soller, *Zeit. Elektrochem.*, **11**. 863, 1903; H. Dercum, *Brit. Pat. No.* 3801, 1898; W. Stein, *Polyt. Centr.*, **36**. 1212, 1869; M. Balanche, *Bull. Soc. Ind. Rouen*, **4**. 419, 1876; R. von Wagner, *Dingler's Journ.*, **227**. 368, 1878; E. Donath, *ib.*, **248**. 72, 1883; E. Bohlig, *Zeit. anal. Chem.*, **9**. 357, 1870; F. Storck and L. L. de Koninck, *Bull. Soc. Ind. Rouen*, **5**. 43, 1877; P. Waage and H. Kämmerer, *Dingler's Journ.*, **227**. 368, 1878; G. Feyerabend, *Chem. Ind.*, **1**. 56, 1878; *Ind. Blätt.*, **15**. 189, 1878; C. K. Potter and F. Robinson, *Brit. Pat. No.* 187636, 1921.

[7] Chemische Fabrik Griesheim-Elektron, *Brit. Pat. No.* 12250, 1901; J. Heibling, *ib.*, 4624, 1898; R. Lorenz, *Zeit. anorg. Chem.*, **12**. 396, 1896; *Zeit. angew. Chem.*, **12**. 1123, 1899.

[8] C. Häussermann, *Dingler's Journ.*, **288**. 93, 111, 161, 1893; D. G. Fitzgerald, *Brit. Pat. No.* 5542, 1886; F. Regelsberger, *Zeit. Elektrochem.*, **6**. 308, 1898; *Zeit. angew. Chem.*, **12**. 1123, 1899; Farbewerke Meister, Lucius, and Brüning, *ib.*, **12**. 1123, 1899; *German Pat., D.R.P.* 103860, 1898; Chemische Fabrik Buckau, *ib.*, 199248, 1906; Höchster Farbwerke, *ib.*, 103860, 1898; L. Darmstädter, *ib.*, 117949, 1899; 138441, 1910; M. le Blanc, *Die Darstellung des Chromes und seiner Verbindungen mit Hilfe das elektrischen Stromes*, Halle a. S., 108, 1902; Easton, Pa., 95, 1904; *Zeit. Elektrochem.*, **7**. 290, 1900; K. Elbs, *ib.*, **6**. 388, 1898; E. Müller and E. Sauer, *ib.*, **18**. 844, 1912; E. Müller and M. Soller, *ib.*, **11**. 863, 1905; M. Soller, *Die Rolle des Bleisuperoxyds als Anode, besonders bei der elektrolytischen Regeneration der Chromsäure*, Halle a. S., 1905; H. R. Carveth and B. E. Curry, *Trans. Amer. Elektrochem Soc.*, **7**. 115, 1905; *Journ. Phys. Chem.*, **9**. 353, 1905; F. Schmiedt, *Beiträge zur electrolytischen Oxydation des Chroms*, Berlin, 1909; A. R. y Miro, *Anal. Fis. Quim.*, **20**. 644, 1922; M. G. Levi and F. Ageno, *Atti Accad. Lincei*, (5), **15**. 549, 615, 1906; R. H. McKee and S. T. Leo, *Journ. Ind. Eng. Chem.*, **12**. 16, 1920; F. W. Skirrow, *Zeit. anorg. Chem.*, **33**. 35, 1903; A. W. Burwell, *U.S. Pat. No.* 1491944, 1924; I. Stscherbakoff, *Zeit. Elektrochem.*, **31**. 360, 1925; I. Stscherbakoff and O. Essin, *ib.*, **33**. 245, 1927; A. Lottermoser and K. Falk, *ib.*, **28**. 366, 1922; R. E. Pearson and E. N. Craig, *Canadian Pat. No.* 221041, 1922; M. de Kay Thompson, *Trans. Amer. Electrochem. Soc.*, **46**. 51, 1924; F. Fichter and E. Brunner, *Journ. Chem. Soc.*, 1862, 1928; M. J. Udy, *U.S. Pat. No.* 1739107, 1929.

§ 3. The Preparation of Chromium

H. N. Warren[1] reduced chromic oxide by heating in a current of *hydrogen* in a tube of compressed lime by means of the oxyhydrogen flame. W. Rohn obtained chromium by reducing chromic oxide at 1500° in a rapid current of hydrogen from which every trace of oxygen and water-vapour had been removed. J. Schilling heated ammonium chromate to whiteness in hydrogen diluted with nitrogen and obtained chromium. M. Billy passed the vapour of the chloride mixed with hydrogen over a boat containing sodium supported on a layer of sodium chloride at 400° to 420°; the hydrogen forms a layer of hydride, and this reduces the chloride, $CrCl_3+3NaH=Cr+3NaCl+3H$. M. A. Hunter and A. Jones reduced the chloride by heating it with sodium in a heavy steel bomb. As previously indicated, L. N. Vauquelin first prepared chromium metal by heating a mixture of chromic oxide and *carbon* in a graphite crucible; and J. B. Richter, and H. Moser obtained it in a similar manner. H. St. C. Deville melted the chromic oxide with not quite sufficient carbon for complete reduction at a temp. of boiling platinum in a lime crucible. According to H. Moissan, chromic oxide is reduced in a few minutes when mixed with carbon and heated in the electric arc furnace. If a large excess of carbon is employed, chromium carbide is formed. If crude chromium in a crucible lined with chromic oxide, and covered with chromic oxide is heated in the arc-furnace, chromium may be obtained free from carbon. If crude chromium is heated with an excess of chromic oxide, the resulting metal is partially oxidized or burnt. Chromium may be obtained with 1·5–1·9 per cent. of carbon by heating the crude metal mixed with lime in an electric furnace. The carbon forms calcium carbide. It is not possible to remove all the carbon by means of lime because, when the proportion of carbon has been reduced below a certain point, an inverse reaction occurs resulting in the formation of crystallized chromium calcium oxide. H. C. Greenwood found that the reduction of chromic oxide by carbon begins at 1180°–1195°, and the reduction is not quantitative. W. B. Hamilton and F. Reid used carbon. W. P. Evans's attempts to obtain chromium from chromyl fluoride, carbon and silica were unsatisfactory. V. and E. Rouff heated an intimate mixture of alkali chromate with silica and carbon to redness, and obtained alkali silicate and chromic oxide which, when intimately mixed with carbon and heated, furnishes chromium. A. Steinberg and A. Deutsch heated to 1000°–1400° a mixture of carbon and an alkaline earth chromate, and obtained chromium. H. Debray showed that if lead chromate be reduced by carbon at a red-heat, lead can be removed from the regulus by means of nitric acid—chromium remains. W. B. Balantine used calcium carbide. J. E. Loughlin heated chromic acid with a mixture of potassium cyanide and carbon. E. Viel obtained chromium from ferro-chromium or other alloys by heating in a high-temp. furnace a mixture of the alloy with an alkaline earth silicate, or with carbon and lime or alumina. E. Kunheim also heated a mixture of chromic sulphate and carbon in an electric arc-furnace, and obtained chromium. A. Binet du Jassonneix found that a mixture of *boron* and chromic oxide in a magnesia crucible heated in the electric arc-furnace furnishes chromium; if a carbon crucible is employed, the chromium always contains carbon. If the chromium boride be heated with copper in an electric furnace, and the product digested with nitric acid, chromium remains. H. Goldschmidt, L. Franck, T. Fujibayashi, and T. Goldschmidt found that chromic oxide can be reduced by the thermite process in which a mixture of chromic oxide and *aluminium* in a crucible is ignited by a fuse. E. Vigouroux, and J. W. Richards said that chromium produced by the thermite process is free from carbon. E. Vigouroux observed that a fairly pure product is formed by heating in a crucible lined with magnesia, a mixture of chromic oxide and 10–20 per cent. chromic anhydride incorporated with the necessary quantity of aluminium powder. A vigorous reaction ensues, and it is over in about a minute. The slag separates readily from the metal. The product contains 0·36–0·40 per cent. of silicon, and 0·74–0·85 per cent. of aluminium and iron. J. Olie used 20 grms. of a mixture of 50 grms. of fused and powdered potassium dichromate and 18 grms. powdered aluminium, together with 10 grms. of a mixture of 450 grms. of calcined chromic oxide and 160 grms. of powdered aluminium. T. Fujibayashi used chromic oxide (100 parts), calcium chromate (10–15 parts), and 90 per cent. of the calculated weight of powdered aluminium. An 85 to 92 per cent. yield was obtained and the resulting chromium contained 3 to 5 per cent. of aluminium. M. Yonezu used a similar process. T. Goldschmidt, M. le Blanc, and G. Döllner used *magnesium*, or a carbide, in place of aluminium in the thermite process; T. Goldschmidt, a mixture of calcium and silicon in place of aluminium; and W. Prandtl and B. Bleyer used a mixture of calcium and aluminium instead of aluminium alone; A. Burger passed the vapour of *calcium* over heated chromic oxide; and heated the product with dil. nitric acid until the acid began to boil; the product was first washed with water, then with alcohol, and finally dried at 100°. He also obtained chromium by heating a mixture of a mol of chromic oxide and 3 gram-atoms of calcium in a sealed tube. B. Neumann reduced chromic oxide with *silicon* in an electric furnace; F. M. Becket used the silicothermic process; S. Heuland reduced the oxide with *calcium silicide;* R. Byman, *ferrosilicon;* D. W. Berlin, an aluminium silicide; R. Saxon, *calcium carbide;* and L. Weiss and O. Aichel, *mischmetall.*

H. Aschermann heated a mixture of chromic and *antimonious oxide* in an electric furnace, and found that the resulting alloy loses all its antimony at a white-heat. S. Heuland melted the chromium ore in an electric furnace with a reducing agent sufficient to produce only a small amount of metal which will contain all the deleterious impurities in the ores, *e.g.*, phosphorus, carbon, or iron. The remainder of the metal is then reduced from the fused slag by addition of calcium silicide. The Metal Research Co. heated in a blast-furnace a mixture of chromic oxide, a sodium compound, and carbon so that the sodium first liberated reduces the chromic oxide to chromium. Processes for the smelting of chrome ores were described by T. R. Haglund, Aktiebolaget Ferrolegeringar, W. Bennett, W. E. S. Strong and co-workers.

F. Wöhler heated in a crucible a mixture of chromic chloride, and zinc along with a mixture of potassium and sodium chlorides; and treated the regulus with dil. nitric acid to remove the zinc. 30 grms. of chromic chloride yielded 6 to 7 grms. of chromium. The process was used by W. Prinz, E. Jäger and G. Krüss, and E. Zettnow; and M. Siewert added that the product is always contaminated with silicon derived from the crucible. F. Wöhler said that there is no advantage in using magnesium or cadmium in place of zinc; but E. Glatzel preferred magnesium. J. J. Berzelius reduced dry chromic chloride with potassium; H. St. C. Deville, sodium; E. Frémy, sodium vapour; K. Seubert and A. Schmidt, magnesium; and L. Hackspill, calcium. H. C. P. Weber heated between 700° to 1200° a mixture of chromic chloride and iron in order to produce metallic chromium and volatilize ferric chloride. If the iron is sufficiently finely divided, and a relatively low temp. is employed for reduction, chromium is obtained in a finely-divided form. If solid pieces of iron are used and the reaction takes place below the m.p. of the metals, a coating of chromium is formed on the pieces of iron. If an excess of iron is used and a sufficiently high temp. is employed, an alloy of chromium and iron is produced. Chlorides of chromium and nickel may be similarly reduced together to form alloys or mixtures with each other or with iron. Chromic oxide may be employed and converted into chloride with carbon and chlorine. The reduction process is advantageously carried out in vacuo or in an inert atm. such as nitrogen. W. P. Evans reduced the vapour of chromyl fluoride by sodium at 400°, and also by zinc near its b.p. Z. Roussin treated a feebly acidic soln. of a chromic salt with sodium amalgam, and heated the resulting chromium amalgam in hydrogen so as to volatilize the mercury. H. Moissan, J. Férée, and C. W. Vincent used a similar process. According to C. Goldschmidt, crystalline chromium is formed when a soln. of, say, chromic nitrate is kept for some days in a tin vessel.

In 1854, R. Bunsen[2] obtained chromium by the electrolysis of an aq. soln. of chromous chloride. He said:

> The density of the current—that is, the strength of the current divided by the surface of the electrode at which the electrolysis occurs—is most important, for, with increasing current density, the power of the current to overcome chemical affinity also increases. For instance, if a current of constant current strength be sent through a soln. of chromic chloride, it depends on the area of the resulting electrode whether hydrogen, chromic oxide, chromous oxide, or chromium is formed. The relative amounts of the constituents of the electrolyte through which the current passes are of no less importance. . . . The reduction to the metal occurs with boiling conc. soln. when the reducing surface receives a current of 0·067 amp. per sq. cm. . . . By using a soln. of chromous chloride, containing some chromic chloride, continuous sheets of chromium can be obtained. These are quite brittle, and the surface lying against the platinum electrode is perfectly white and of a metallic lustre. Chemically pure chromium can be obtained only in this way. It resembles iron very much in external appearance, but it is more permanent in damp air, and when heated burns to chromic oxide. Hydrochloric and sulphuric acids dissolve it slowly to chromous salts with the evolution of hydrogen; and it is scarcely attacked by nitric acid even when boiling. . . . If the current density be gradually lowered, a point is soon reached when in place of the metal, there is a copious formation of anhydrous chromous-chromic oxide. This oxide can be made only in this way, and it is purified by long boiling with aqua regia. It is a black crystalline powder, soluble in no acid, and burning in air like pyrophoric iron with a lively deflagration, to form green chromic oxide. Its composition varies between Cr_4O_5 and Cr_5O_6—*vide infra*, chromic chromate.

According to E. Müller and P. Ekwall, in the electrolysis of a soln. of chromic acid using a carbon cathode, a film of chromic chromate begins to form at a potential, measured against a normal calomel electrode, of +0·8 volt, while evolution of hydrogen begins at about —1·2 volt. With a platinum electrode, hydrogen evolution begins at about 0·4 volt, while the separation of chromium, which is contaminated with oxide, occurs at about —1·2 volt, and is preceded by the formation of the insoluble, colloidal chromic chromate film, which is first observed microscopically at —0·7 volt, and is pressed cataphoretically to the cathode. The gel is purified by dialysis, and is found to migrate to the cathode, where it is coagulated. The compound is soluble in acids and bases, and its composition corresponds to the formula $Cr_2(OH)_4CrO_4$. When present as a film, the molecules are oriented and form a diaphragm, which is impervious to CrO_4'' or $HCrO'_4$-ions, but allows $H^{\cdot}$-ions to pass. Reaction accordingly ceases until the hydrogen separation potential is exceeded when the film is broken and the reaction proceeds in accordance with the equation: $Cr_2(OH)_4CrO_4+2H_2CrO_4=2Cr^{\cdots}+3CrO_4''+4H_2O$. Deposition of chromium then occurs, and the chromic chromate film is again formed. The deposition of successive layers of this film according to the magnitude of the applied potential is shown under the microscope by differences in colour. The presence of sulphuric acid in the electrolyte modifies the film formation and increases the intervals of exposure of the electrode, whereby greater accession of chromium ions results, while contamination of the deposited metal with oxide is suppressed. M. L. V. Gayler used a one per cent. sulphuric acid soln. of chromic acid. E. Müller and J. Stscherbakoff found that in spite of its strong oxidizing action, pure chromic acid is not electrolytically reducible in aq. soln., but it becomes so on addition of SO''_4-ions. They showed that the cathode becomes coated with an invisible, non-conducting, fine-grained layer, which prevents the reduction of chromic acid. This layer becomes charged in presence of SO''_4, but this occurs only after a certain cathode potential has been attained. It is hence concluded that charging by the SO''_4-ions necessitates the electrostatic attraction of these ions by the layer of colloid. S. Takegami also studied the deposit of colloidal chromic oxide.

R. Bunsen suggested that it would be worth trying to find if allotropic forms of chromium could be produced by electrolyzing green and blue chromic salt soln. Subsequent work, however—by W. R. Whitney, etc.—has shown the hypothesis to be untenable. S. O. Cowper-Coles obtained a bright deposit of chromium from a soln. of 25 parts of chromic chloride in 75 parts of water at 88°, with a current of 0·04–0·05 amp. per sq. cm. With a cold soln., gas is evolved at both electrodes, but no metallic deposit is obtained until an excess of hydrochloric acid is added. J. Férée found that a steel-grey deposit of chromium on a platinum cathode is formed with a soln. of chromic chloride acidified with hydrochloric acid; and a silver-white deposit from a soln. containing potassium and chromic chlorides in the proportion of 1 : 3, and a current density of 0·15 amp. per sq. cm., and 8 volts. J. Voisin added that when the deposit is over 3 or 4 mm. thick, it is liable to peel off. The Wolfram-Lampen A. G. obtained chromium by the electrolysis of soln. of chromic chloride in acetone; J. Roudnick, and G. Neuendorff and F. Sauerwald, by the electrolysis of the fused silicate.

S. O. Cowper-Coles found that a soln. of 100 parts of chrome-alum in 100 parts of water with 12 parts of barium sulphate does not yield a deposit of chromium metal on electrolysis. E. Placet found that when a soln. of chrome-alum and an alkali sulphate acidified with sulphuric acid, is electrolyzed, chromium is deposited at the cathode as a hard, bluish-white, lustrous metal, which, under certain conditions, crystallizes in groups resembling the branching of firs. Other metals and alloys—bronze, copper, iron, brass, etc.—may be plated with chromium, and a surface can be obtained to resemble oxidized silver. E. Placet and J. Bonnet have a number of patents on this subject.

Various baths have been recommended and the subject of chromium plating has been discussed by M. Alkan, J. D. Alley, C. M. Alter and F. C. Mathers, R. Appel, P. Askenasy and A. Révai, E. M. Baker and E. E. Pettibone, E. M. Baker and A. M. Rente, M. Ballay,

J. Bauer, F. M. Becket, R. Bilfinger, W. Birett, J. Blasberg, W. Blum, J. J. Bloomfield and W. Blum, G. le Bris, A. Champion, A. Butziger, Chemical Treatment Co., Chromium Corporation of America, A. J. Coignard, J. Cournot, W. Crafts, J. W. Cuthbertson, G. J. Delatre, S. Dreyfus, W. S. Eaton, C. H. Eldridge, P. W. Ellwanger, G. M. Enos, D. T. Ewing and A. K. Malloy, H. L. Farber and W. Blum, S. Field, C. G. Fink, C. G. Fink and C. H. Eldridge, J. H. Frydlender, G. P. Fuller, G. Fuseya and co-workers, G. E. Gardam, R. Grah, A. K. Graham, L. E. and L. F. Grant, F. Grove-Palmer, G. Grube, C. A. Guidini, O. Günther, O. Hahn, C. Hambuechen, J. Harden and H. T. Tillquist, H. E. Haring, H. E. Haring and W. P. Barrows, J. Hausen, E. V. Hayes-Gratze, J. M. Hosdowich, M. Hosenfeld, H. W. Howes, W. E. Hughes, T. W. S. Hutchins, V. P. Ilinsky and co-workers, R. Justh, E. Kalmann, Y. Kato and co-workers, D. B. Keyes and S. Swann, D. M. Killeffer, V. Kohlschütter and A. Good, E. Krause, F. Krupp, E. Kruppa, S. Kyropoulos, H. Lange, F. Lauterbach, E. Liebreich and co-workers, H. Leiser, P. Leistritz and F. Burghauser, B. F. Lewis, C. L. Long and co-workers, F. Longauer, H. S. Lukens, O. Macchia, J. F. K. McCullough and B. W. Gilchrist, D. J. MacNaughton and co-workers, B. Mendelsohn, Metal and Thermite Corporation, Metropolitan-Vickers Electrical Co., E. Müller, E. Müller and co-workers, M. Nagano and A. Adachi, National Electrolytic Co., W. Obst, Olausson and Co., E. A. Ollard, K. Oyabu, A. H. Packer, A. V. Pamfiloff and G. F. Filippuicheff, L. C. Pan, J. C. Patten, W. Pfanhauser, W. M. Phillips, W. M. Phillips and M. F. Macaulay, W. M. Phillips and P. W. C. Strausser, H. C. Pierce, H. C. Pierce and C. H. Humphries, R. J. Piersol, W. L. Pinner, W. L. Pinner and E. M. Baker, F. R. Porter, H. E. Potts, C. H. Procter, E. Richards, J. G. Roberts, J. Roudnick, G. F. Sager, F. Salzer, G. J. Sargent, V. Schischkin and H. Gernet, H. Schmidt, R. Schneidewind and co-workers, K. W. Schwartz, A. Siemens, E. W. M. von Siemens and J. G. Halske, J. Sigrist and co-workers, O. J. Sizelove, J. Stscherbakoff and O. Essin, W. Steinhorst, L. E. Stout and J. Carol, F. Studinges, H. E. Sunberg, V. Szidon, O. P. Watts, L. Weisberg and W. F. Greenwald, S. Wernick, H. Wolff, M. Wommer, L. Wright, F. W. Würker, and S. Yentsch.

J. F. L. Möller and E. A. G. Street obtained chromium by the electrolysis of an aq. soln. of chrome-alum and sodium sulphate at 90° with a current density of 0·4 amp. per sq. cm. R. Stahn electrolyzed soln. of chromous salts. J. Voisin also obtained no deposit of chromium with a violet soln. of chrome-alum mixed with potassium hydrosulphate, using a current density of 0·02 to 0·20 amp. per sq. cm. and 4 to 12 volts, and similarly with neutral and alkaline soln.; with a green soln. of chrome-alum and 0·18 amp. per sq. cm. a small, grey deposit of a substance soluble in hydrochloric acid was obtained. According to M. le Blanc, chromium deposits cannot be obtained in the manner described. Among other processes, the following can be used:

A sat. soln. of chromic sulphate at the temp. of the room, was used and 100 c.c. dil. to 600 c.c. with water and then sodium chloride added to saturation. A platinum foil was used as cathode. With 40 sq. cm. active cathode surface, using a current density of 0·2 amp. per sq. cm., there was obtained a quite small, black precipitate which from its behaviour appeared to be chromium. With a current density of 0·3 amp. per sq. cm. no precipitate was obtained. A precipitate did not appear when the above bath was sat. with sodium sulphate instead of sodium chloride and electrolyzed at 30° and 80° with a current of 0·2 and 0·3 amp. per sq. cm.

F. Adcock found that chromium of a high degree of purity can be obtained by the electrolysis of an aq. soln. containing 30 per cent. of purified chromic acid, and one per cent. sulphuric acid using tin or steel cathodes. In one with a steel cathode rotating 30 revs. per minute, the temp. of the bath was 20°, the voltage 5·2, and the amperage 140. The current densities at the cathode and anode were 28 amp. and 7·2 amp. per sq. dm., and the yield of chromium in 30 hrs. was 500 grms., with a current consumption of 8·3 ampère-hrs. per gram. All the samples as deposited contained hydrogen and oxygen, the former being liberated during remelting in vacuo. The cathode chromium is in a form which leaves no residue on dissolution in acid, and is converted, when heated in vacuo, into insoluble chromic oxide. This can be removed, however, by heating the solid metal in purified and dried hydrogen to 1500°–1600°. After these treatments, spectroscopic examination failed to reveal any impurities. T. Murakami studied the action of chemical reagents on the deposits.

B. Neumann and G. Glaser examined the influence of current strength, current density, conc., and temp. with different soln. of chromic salts. The diaphragm cells contained the chromium salt soln. in the cathode compartment, and a mineral acid or salt soln. in the anode chamber. The cathode was ordinary carbon, but the deposited chromium was found to adhere also to cathodes of borax, lead, or platinum; the anode, according to the soln. employed, was lead, platinum, or carbon. If the cathode soln. is not well circulated, it becomes impoverished at the cathode, and with high current densities only the chromosic oxide is deposited. Using a chromic chloride soln. with 100 grms. of Cr per litre, at the temp. of the room, and with current densities less than 0·072 amp. per sq. cm., the deposit consisted of metal mixed with more or less of the chromosic oxide; and with current densities 0·091 to 0·182 amp. per sq. cm., metal alone was deposited with a 38·4 to 38·6 per cent. ampère output. The deposit is good up to about 50°, but beyond that the chromium deposits as a black powder. With a constant current density and with soln. containing 184 grms. of Cr per litre and over, the deposit was a metallic powder; with soln. containing respectively 158, 135, and 105 grms. of Cr per litre, the percentage ampère outputs of pure metal were respectively 50·6, 49·0, and 38·4; with soln. containing 179 grms. of Cr per litre, at first metal and the chromosic oxide were deposited; and with 53 or less grms. of Cr per litre, chromosic oxide and hydrogen were formed. Sulphate and acetate soln. give similar results except the numerical values differed from those just indicated. The acetate soln. gave imperfect precipitates, and poor yields; the best yield—84·6 per cent.—with sulphate soln. occurred with soln. containing 65–85 grms. of Cr per litre, and a current density of 0·13 to 0·20 amp. per sq. cm. B. Neumann, and G. Glaser concluded that the influence of temp. is of slight importance, but H. R. Carveth and W. R. Mott found that with chloride soln. a rise of temp. caused a marked decrease in efficiency. The electrodeposition of chromium was also investigated by J. Sigrist and co-workers, and E. F. Smith. S. Kyropoulos found that chromium is deposited more freely in isolated spots on the crystal faces of tempered aluminium. A higher current density favours deposition on the crystal faces. Deposition on the crystal faces is favoured by conditions such that the production of hydrogen at the cathode is possible. Resistance to copper deposition is most clearly shown by passive chromium, deposition occurring only on isolated spots of non-passive chromium; with hydrogen evolution at the cathode, deposition occurs on the crystal faces of the chromium.

According to H. R. Carveth and W. R. Mott, in the electrolysis of a soln. of chromic chloride containing 100 grms. of Cr per litre, at 21°, and a current density of 0·5 amp. per sq. cm., the efficiency slowly increased until a constant value of about 30 per cent. was attained. This phenomena was attributed to the formation of chromous chloride which is assumed to be necessary for efficient electrolysis—raising the temp. acts deleteriously by increasing the rate of oxidation of chromous chloride. The bubbling of air through the soln. diminished the efficiency. Variations in the nature of the anode liquid caused considerable alterations in the efficiency; high values were obtained with an anolyte of ammonium sulphate, due, it is supposed, to diffusion into the cathode chamber. O. Dony-Hénault added that the formation of chromous chloride is not the only condition required for the deposition of chromium from a soln. of chromic salt. During the electrolysis of a soln. of chrome-alum, the green soln. becomes violet, and after a time deposits violet crystals of the alum. Chromium was deposited from the violet but not from the green soln.

According to J. Voisin, the electrolysis of a soln. of purified chromic acid gives 2 vols. of hydrogen and one vol. of oxygen as in the analogous case of sulphuric acid. The electrolysis of a soln. of ordinary chromic acid—260 grms. per litre—with a current density of 0·40 amp. per sq. cm. gives 0·250 grm. of white, adherent chromium per hour. Chromium anodes are preferable. The deposit is improved when 5–6 grms. of boric acid per litre are present. A sat. soln. of chromic hydroxide in hydrofluoric acid, and a current density of 0·2 to 0·20 amp. per sq. cm. and 12 volts gives no metal, but a green deposit of $Cr_2O_3.9H_2O$ appears on the cathode.

H. R. Carveth and B. E. Curry found that chromium begins to be deposited instantly from a soln. of impure chromic acid at 18° with a current density of about 0·80 amp. per sq. cm. The deposition is not so readily obtained with soln. of purified chromic acid which has a decomposition voltage of 2·31 volts. In all cases, the liquid was coloured brown, and chromic salts were produced; the brown precipitate formed at the cathode is probably $Cr(CrO_4)$. It is assumed that sexivalent chromium cations are present in the soln. of chromic acid, and that the increased deposition which occurs when sulphuric acid is present, is due to an increase in the conc. of the sexivalent Cr-cations by a reaction of chromic acid with the sulphuric acid. F. Salzer found that the deposits of chromium are produced with a bath of approximately equal proportions of chromic acid and chromic oxide; or preferably with an excess of chromic acid. The quantities should be kept nearly constant during the electrolysis, and the temp. maintained constant by cooling the bath. Anodes, capable of oxidizing the chromium oxide to chromic acid during the passage of the current, may be employed, in order to maintain a constant composition in the bath by compensating for the chromic acid reduced at the cathode, or insoluble anodes, such as lead or platinum, may be used to maintain a constant composition, these being in part freely suspended in the bath, and in part separated from the cathode chamber by convenient diaphragms. The subject was investigated by E. Liebreich, E. Müller, E. Müller and P. Ekwall, and G. Grube and G. Breitinger.

A. Krupp prepared chromium of a high degree of purity by electrolyzing a fused chromium halide using impure chromium as anode. The electrodeposition of chromium has been investigated by R. Appel,[3] C. L. Long and co-workers, G. Neuendorff and F. Sauerwald, and F. Andersen. R. Taft and H. Barham studied the electrodeposition of chromium from soln. of its salts in liquid ammonia.

H. Moissan, and J. Férée prepared *pyrophoric* chromium by distilling the amalgam in vacuo at 300°, but if heated more strongly, it loses its pyrophoric activity. H. Küzel obtained **colloidal chromium** by bringing the element to a fine state of subdivision by grinding, or by cathodic disintegration. It was then converted into the colloidal state by repeated alternate treatments for long periods with dil. acid soln. and dil. alkaline or neutral soln., under the influence of moderate heat and violent agitation. After each treatment the material was washed with distilled water or other solvent until completely free from the reagent employed. T. Svedberg also prepared **chromium hydrosol** by his process of cathodic disintegration; and with isobutyl alcohol as the liquid menstruum, **chromium** *iso***butylalcosol** was obtained. G. Bredig did not obtain much success with splutterings from an electric arc under water.

REFERENCES.

[1] L. N. Vauquelin, *Journ. Phys.*, **45**. 393, 1794; **46**. 152, 311, 1798; *Journ. Mines*, **6**. 737, 1797; *Nicholson's Journ.*, **2**. 387, 441, 1799; *Phil. Mag.*, **1**. 279, 361, 1798; **2**. 74, 1798; *Ann. Chim. Phys.*, (1), **25**. 21, 194, 1798; (1), **70**. 70, 1809; J. B. Richter, *Ueber die neueren Gegenstände der Chymie*, Breslau, **10**. 30, 1802; *Gehlen's Journ.*, **5**. 351, 1805; M. le Blanc, *Die Darstellung des Chrome und seiner Verbindungen mit Hilfe des elektrischen Stromes*, Halle a. S., 108, 1902; Easton, Pa., 95, 1904; *Zeit. Elektrochem.*, **7**. 290, 1900; H. St. C. Deville, *Ann. Chim. Phys.*, (3), **46**. 182, 1856; *Compt. Rend.*, **44**. 676, 1857; M. Billy, *ib.*, **158**. 578, 1914; E. Vigouroux, *ib.*, **141**. 722, 1906; *Bull. Soc. Chim.*, (4), **1**. 10, 1906; L. Hackspill, *ib.*, (4), **1**. 896, 1907; Z. Roussin, *Journ. Pharm. Chim.*, (4), **3**. 413, 1866; *Bull. Soc. Chim.*, (2), **6**. 93, 1866; H. Moissan, *ib.*, (2), **31**. 149, 1879; (3), **11**. 13, 1894; *Ann. Chim. Phys.*, (5), **21**. 249, 1880; *Compt. Rend.*, **88**, 180, 1879; **116**. 349, 1893; **117**. 679, 1893; **119**. 187, 1894; A. Binet du Jassonneix, *ib.*, **143**. 897, 1906; **144**. 915, 1907; E. Frémy, *ib.*, **44**. 633, 1857; J. Férée, *ib.*, **121**. 822, 1895; W. Prinz, *ib.*, **116**. 392, 1893; K. Seubert and A. Schmidt, *Liebig's Ann.*, **267**. 239, 1892; F. Wöhler, *ib.*, **111**. 230, 1859; L. Weiss and O. Aichel, *ib.*, **337**. 370, 1904; H. Goldschmidt, *ib.*, **301**. 19, 1898; *Zeit. Elektrochem.*, **4**. 494, 1898; *Journ. Soc. Chem. Ind.*, **17**. 543, 1898; C. Goldschmidt, *Chem. Ztg.*, **29**. 56, 1905; T. Goldschmidt, *German Pat., D.R.P.* 96317, 112486, 1895; 175885, 187457, 1905; G. Döllner, *ib.*, 113037, 1897; H. Aschermann, *ib.*, 93744, 1896; E. Viel, *ib.*, 205789, 1907; V. and E. Rouff, *ib.*, 42213, 1887; A. Steinberg and A. Deutsch, *ib.*, 69704, 1890; J. Schilling, *ib.*, 32750, 1909; *Zeit. angew. Chem.*, **24**. 910, 1911; W. P. Evans, *ib.*, **4**. 18, 1891; H. N. Warren, *Chem. News*, **70**. 102, 1894; R. Saxon, *ib.*, **137**. 216, 1928; A. R. y Miro, *Anal. Fis. Quim.*, **20**. 644, 1922; M. Siewert, *Zeit. ges. Naturwiss.*, **17**. 536, 1861; H. Debray in

A. Wartz, *Dictionnaire de chimie pure et appliquée*, Paris, **1**. 885, 1867 ; E. Jäger and G. Krüss, *Ber.*, **22**. 2052, 1889 ; E. Glatzel, *ib.*, **23**. 3127, 1890 ; T. Fujibayashi, *Journ. Japan. Chem. Ind.*, **25**. 499, 1922 ; J. E. Loughlin, *Amer. Journ. Science*, (2), **45**. 131, 1868 ; H. Moser, *Chemische Abhandlung über das Chrom*, Wien, 1824 ; *Schweigger's Journ.*, **42**. 99, 1824 ; L. Franck, *Chem. Ztg.*, **22**. 236, 1898 ; W. Rohn, *Zeit. Metallkunde*, **16**. 275, 1924 ; E. Zettnow, *Pogg. Ann.*, **143**. 477, 1871 ; J. Olie, *Chem. Weekbl.*, **3**. 662, 1906 ; J. J. Berzelius, *Liebig's Ann.*, **49**. 247, 1844 ; *Handl. Akad. Stockholm*, 1, 1843 ; *Pogg. Ann.*, **61**. 1, 1844 ; *Taylor's Scient. Memoirs*, **4**. 240, 1846 ; C. W. Vincent, *Phil. Mag.*, (4), **24**. 328, 1862 ; H. C. P. Weber, *U.S. Pat. No.* 1373038, 1921 ; Metal Research Co., *ib.*, 1581698, 1926 ; W. Bennett, *ib.*, 1441479, 1923 ; W. B. Hamilton and F. Reid, *ib.*, 1520240, 1924 ; W. E. S. Strong, C. E. Parsons and S. Peacock, *ib.*, 1581698, 1920 ; I. Stscherbakoff and O. Essin, *Zeit. Elektrochem.*, **32**. 396, 1926 ; S. Heuland, *French Pat. No.* 602448, 1925 ; D. W. Berlin, *Brit. Pat. No.* 193057, 1923 ; T. R. Haglund, *ib.*, 232549, 239404, 1924 ; Aktiebolaget Ferrolegeringar, *ib.*, 163263, 1921 ; W. B. Ballantine, *ib.*, 152399, 1919 ; M. A. Hunter and A. Jones, *Trans. Amer. Electrochem. Soc.*, **44**. 23, 1923 ; R. Byman, *Jernkontorets Ann.*, **107**. 106, 1923 ; M. Yonezu, *Japan. Pat. No.* 36882, 1920 ; J. W. Richards, *Met. Chem. Engg.*, **15**. 26, 1916 ; *Trans. Amer. Inst. Chem. Eng.*, **9**. 92, 1916 ; H. C. Greenwood, *Journ. Chem. Soc.*, **93**. 1488, 1908 ; A. Burger, *Reduktion durch Calcium*, Basel, 7, 1907 ; B. Neumann, *Zeit. Elektrochem.*, **14**. 169, 1908 ; *Stahl Eisen*, **28**. 356, 1908 ; W. Prandtl and B. Bleyer, *Zeit. anorg. Chem.*, **64**. 223, 1909 ; E. Kunheim, *Ueber die Einwirkung des Lichtbogens auf Gemische von Sulfaten mit Kohle*, Berlin, 39, 1900 ; F. M. Beckett, *Canada Pat. No.* 302100, 1930.

[2] R. Bunsen, *Pogg. Ann.*, **91**. 619, 1854 ; *Ann. Chim. Phys.*, (3), **41**. 354, 1854 ; S. O. Cowper-Coles, *Chem. News*, **81**. 16, 1900 ; J. Férée, *Bull. Soc. Chim.*, (3), **25**. 617, 1901 ; *Compt. Rend.*, **121**. 823, 1895 ; L. Weisberg and W. F. Greenwald, *Amer. Metal Ind.*, **25**. 457, 1927 ; S. Takegami, *Bull. Japan. Chem. Soc.*, **4**. 156, 1929 ; R. Stahn. *Ein Beitrag zur Chemie des zweiwertigen Chroms*, Berlin, 1926 ; W. R. Whitney, *Zeit. phys. Chem.*, **20**. 40, 1896 ; E. Placet, *Compt. Rend.*, **115**. 945, 1892 ; E. Placet and J. Bonnet, *Brit. Pat. No.* 19544, 1890 ; 22854, 22855, 22856, 1891 ; 6751, 1893 ; *German Pat., D.R.P.* 66099, 1890 ; A. Krupp, *ib.*, 81225, 1893 ; E. Viel, *ib.*, 205789, 1907 ; F. Salzer, *Zeit. Elektrochem.*, **33**. 309, 1927 ; *Brit. Pat. No.* 1344, 1908 ; *Austrian Pat. No.* 48306, 1911 ; *German Pat., D.R.P.* 221472, 1907 ; 225769, 1909 ; Wolfram-Lampen A. G., *ib.*, 237014, 1910 ; J. F. L. Möller and E. A. G. Street, *ib.*, 105847, 1898 ; *Brit. Pat. No.* 18743, 1898 ; G. le Bris, *ib.*, 243667, 1924 ; E. Liebreich, *ib.*, 164731, 1921 ; 243046, 1924 ; *Zeit. Metallkunde*, **14**. 367, 1922 ; **16**. 175, 1924 ; *Zeit. Elektrochem.*, **27**. 94, 1921 ; **29**. 208, 1923 ; **33**. 69, 1927 ; **34**. 41, 1928 ; *Amer. Metal Ind.*, **21**. 109, 1921 ; *Korrosion Metallschutz*, **2**. 38, 1926 ; *Metallwaren Ind.*, **24**. 68, 1926 ; R. Bilfinger, *ib.*, **24**. 7, 28, 51, 108, 1920 ; H. Lange, *ib.*, **24**. 167, 1926 ; E. Kruppa, *ib.*, **24**. 50, 1926 ; M. Alkan, *ib.*, **24**. 327, 1926 ; W. Pfanhauser, *ib.*, **24**. 347, 1926 ; *Das Verchromungsverfahren*, Leipzig, 1926 ; *Chem. Ztg.*, **47**. 581, 1923 ; **53**. 207, 1929 ; B. Neumann and G. Glaser, *Zeit. Elektrochem.*, **7**. 656, 1901 ; E. Müller, *ib.*, **32**. 399, 1926 ; **33**. 72, 1927 ; E. Müller and P. Ekwall, *ib.*, **35**. 84, 1929 ; E. Müller and J. Stscherbakoff, *ib.*, **35**, 222, 1929 ; E. Müller and O. Essin, *ib.*, **36**. 2, 1930 ; G. Grube and G. Breitinger, *ib.*, **33**. 112, 1927 ; V. Kohlschutter and A. Good, *ib.*, **33**. 277, 1927 ; V. Schischkin and H. Gernet, *ib.*, **34**. 57, 1928 ; O. Dony-Hénault, *ib.*, **12**. 329, 1906 ; K. Liebreich and V. Duffek, *Ber.*, **62**. B, 2527, 1929 ; P. Askenasy and A. Révai, *ib.*, **19**. 344, 1913 ; H. Goldschmidt, *ib.*, **7**. 656, 1901 ; J. Roudnick, *ib.*, **35**. 249, 1929 ; *Bull. Soc. Chim. Belg.*, **38**. 276, 1929 ; E. F. Smith, *Journ. Amer. Chem. Soc.*, **27**. 1265, 1905 ; H. R. Carveth and W. R. Mott, *Journ. Phys. Chem.*, **9**. 231, 1905 ; H. R. Carveth and B. E. Curry, *ib.*, **9**. 353, 1905 ; C. G. Fink, *Forging*, **11**. 202, 1925 ; S. Field, *Metal Ind.*, **30**. 266, 1927 ; J. Voisin, *Rev. Mét.*, **7**. 1137, 1910 ; F. W. Würker, *French Pat. No.* 67829, 1925 ; M. le Blanc, *Die Darstellung des Chroms und seiner Verbindungen mit Hilfe des elektrischen Stromes*, Halle a. S., 1902 ; Easton, Pa., 1904 ; G. J. Sargent, *Trans. Amer. Electrochem. Soc.*, **37**. 479, 1920 ; C. L. Long, D. J. Macnaughton, and G. P. Gardam, *Brit. Pat. No.* 258, 724, 1925 ; J. D. Alley, *ib.*, 258242, 1925 ; C. G. Fink, *ib.*, 258594, 1925 ; 275223, 1926 ; H. E. Sunberg, *ib.*, 274913, 1926 ; M. Hosenfeld, *Siemens' Zeit.*, **7**. 439, 1927 ; J. Sigrist, P. Winkler, and M. Wantz, *Helvetica Chim. Acta*, **7**. 968, 1924 ; S. Kyropoulos, *Zeit. anorg. Chem.*, **119**. 299, 1921 ; F. C. Kelly, *Brass World*, **19**. 291, 1923 ; *Metal Ind.*, **23**. 385, 1923 ; K. W. Schwartz, *ib.*, **23**. 367, 369, 1923 ; **25**. 149, 1924 ; *Trans. Amer. Electrochem.*, **44**. 451, 1923 ; *Canada Pat. No.* 282730, 1928 ; *U.S. Pat. No.* 1589988, 1926 ; 1720354, 1929 ; S. Kyropoulos, *ib.*, 1590101, 1926 ; Y. Kato and T. Murakami, *Journ. Japan. Soc. Chem. Ind.*, **31**. 124, 1928 ; Y. Kato, T. Murakami and S. Saito, *ib.*, **31**. 128, 1928 ; H. W. Howes, *Glass Rev.*, **3**. 12, 1927 ; S. Yentsch, *Metallwaren Ind.*, **25**. 147, 1927 ; F. Longauer, *Magyar Mernök Epites. Közl.*, **62**. 49, 1928 ; H. Schmidt, *German Pat., D.R.P.* 472157, 1926 ; G. Grube, *ib.*, 454168, 1921 ; W. Steinhorst, *ib.*, 476264, 1927 ; G. J. Delatre, *French Pat. No.* 647248, 1927 ; G. E. Gardam, *Metal. Ind.*, **34**. 299, 1929 ; D. T. Ewing and A. K. Malloy, *Bull. Michigan Eng. Exp. Station*, 7, 1926 ; A. K. Graham, *Amer. Metal Ind.*, **35**. 18, 1928 ; G. F. Sager, *A Study of the Production of Chromium Surfaces for Retarding the Corrosion of Nickel at High Temperatures*, New York, 1927 ; E. V. Hayes-Gratze, *Brit. Pat. No.* 300043, 1928 ; H. E. Potts, *ib.*, 292094, 1928 ; J. Cournot, *Mém. Comp. Rend. Soc. Ing. Civils*, 303, 1928 ; *Usine*, **37**. 21, 1928 ; F. M. Becket, *U.S. Pat. No.* 1720312, 1929 ; C. M. Alter and F. C. Mathers, *Trans. Amer. Electrochem. Soc.*, **56**. 363, 1929 ; *Metal Ind.*, **35**. 545, 1929 ; W. Birett, *Zeit. Metallkunden*, **21**. 372, 1929 ; *Metals Alloys*, **1**. 452, 1930 ; C. A. Guidini, *Schweiz. Apoth. Ztg.*, **67**. 87, 1929 ; *Journ. Pharm. Alsace-Lorraine*, **56**. 78, 1929 ; V. Szidon, *Brit. Pat. No.* 320440, 320952, 1928 ; F. Andersen, *Ueber die Darstellung einiger*

Schwermetalle und Legierungen durch Elektrolyse im Schmelzfluss, Darmstadt, 1916 ; J. M. Hosdowich, *U.S. Pat. No.* 1590170, 1926 ; *Brit. Pat. No.* 256572, 1925 ; *Amer. Metal Ind.*, **21**. 441, 1923 ; R. Schneidewind, *ib.*, **32**. 140, 1928 ; *Bull. Univ. Michigan Eng. Research*, 8, 1927 ; 10, 1928 ; 3, 1930 ; P. Schneidewind and G. F. Urban, *Trans. Amer. Electrochem. Soc.*, **53**. 457, 1928 ; R. Schneidewind, G. F. Urban and R. C. Adams, *ib.*, **53**. 499, 1928 ; E. Kalmann, *Metallbörse*, **15**. 503, 1925 ; K. Oyabu, *Zeit. Elektrochem.*, **29**. 491, 1923 ; J. Stscherbakoff and O. Essin, *ib.*, **33**. 245, 1927 ; C. H. Proctor, *Rev. Amer. Electroplater's Soc.*, **16**. 23, 1929 ; *Metal Cleaning*, **1**. 349, 507, 1929 ; *Metals Alloys*, **1**. 474, 1929 ; *Brass World*, **23**. 193, 1927 ; W. E. Hughes, *Beama*, **10**. 138, 1922 ; Olausson and Co., *French Pat. No.* 612880, 1926 ; *Brit. Pat. No.* 264442, 1926 ; S. Wernick, *Elect. Times*, **78**. 149, 1930 ; *Ind. Chemist*, **5**. 524, 1929 ; *Metal Ind.*, **31**. 291, 313, 345, 1927 ; L. Wright, *ib.*, **31**. 577, 1927 ; W. Pfaundler, *ib.*, **31**. 315, 1927 ; O. P. Watts, *ib.*, **31**. 563, 1927 ; L. E. and L. F. Grant, *Trans. Amer. Electrochem. Soc.*, **53**. 509, 1928 ; O. Günther, *Apparatebau*, **39**. 4, 1926 ; B. Mendelsohn, *Motorwagen*, **28**. 728, 1925 ; W. Blum, *Iron Age*, **118**. 1685, 1926 ; *Amer. Mach.*, **65**. 948, 1926 ; *Brass World*, **22**. 381, 1926 ; *Metal Ind. New York*, **25**. 14, 1927 ; *Mech. Eng.*, **49**. 33, 1927 ; **50**. 927, 1928 ; Metropolitan-Vickers Electrical Co., *Brit. Pat. No.* 258242, 1926 ; Chromium Corporation of America, *ib.*, 258594, 1926 ; J. C. Patten, *ib.*, 282337, 1927 ; H. C. Pierce and C. H. Humphries, *Canadian Pat. No.* 266323, 1926 ; W. Crafts, *Carnegie Mem. Iron. Steel Inst.*, **15**. 175, 1926 ; Chemical Treatment Co., *U.S. Pat. No.* 1581188, 1926 ; G. P. Fuller, *ib.*, 1531088, 1925 ; C. Hambuechen, *ib.*, 1544451, 1925 ; H. Wolff, *German Pat., D.R.P.* 422461, 1923 ; E. W. von Siemens and J. G. Halske, *ib.*, 436084, 1925 ; *Brit. Pat. No.* 259900, 259924, 1926 ; 286451, 1927 ; *French Pat. No.* 638283, 1927 ; M. Wommer, *ib.*, 635699, 635700, 636424, 1927 ; J. Harden and H. T. Tillquist, *Brit. Pat. No.* 259761, 1925 ; C. G. Fink and C. H. Eldridge, *Iron Age*, **121**. 1680, 1928 ; *Brit. Pat. No.* 260154, 1926 ; R. Appel, *ib.*, 259118, 265833, 274882, 1926 ; 1713514, 1929 ; W. S. Eaton, *ib.*, 284900, 1927 ; F. W. Würker, *ib.*, 266045, 1925 ; R. Grah, *U.S. Pat. No.* 1542549, 1925 ; *Brit. Pat. No.* 223611, 1923 ; A. J. Coignard, *ib.*, 224065, 1923 ; O. Hahn, *ib.*, 238551, 1925 ; T. W. S. Hutchins, *ib.*, 239977, 1924 ; F. Krupp, *ib.*, 197887, 1922 ; National Electrolytic Co., *ib.*, 226066, 1924 ; Metal and Thermite Corporation, *U.S. Pat. No.* 1496231, 1496232, 1924 ; H. C. Pierce and C. H. Humphries, *ib.*, 1545196, 1925 ; H. C. Pierce, *ib.*, 1645927, 1927 ; *Brit. Pat. No.* 267080, 1926 ; J. Sigrist, P. Winkler and M. Wantz, *Helvetica Chim. Acta*, **7**. 968, 1924 ; E. Richards, *Metalltechnik*, **51**. 182, 1926 ; F. R. Porter, *Brass World*, **23**. 267. 1927 ; *Metal Ind. Amer.*, **25**. 375, 1927 ; G. M. Enos, *Trans. Amer. Electrochem. Soc.*, **48**. 37, 1925 ; *Metal Ind.*, **27**. 261, 1925 ; *Brass World*, **21**. 277, 1925 ; H. E. Haring and W. P. Barrows, *Electrodeposition of Chromium from Chromic Acid Baths*, Washington, 1927 ; *Tech. Paper U.S. Bur. Standards*, **21**. 413, 1927 ; H. E. Haring, *Chem. Met. Engg.*, **32**. 692, 1925 ; *Brass World*, **21**. 395, 1925 ; *Metal Ind.*, **27**. 310, 1925 ; *Amer. Metal Ind.*, **24**. 68, 1926 ; E. A. Ollard, *Korrosion Metallschutz*, **4**. 208, 1928 ; *Elektroplat. Deposit. Tech.*, 5, 1927 ; *Chim. Ind.*, **21**. 321, 1929 ; *Brass World*, **22**. 119, 1926 ; **23**. 497, 1925 ; *Metal Ind.*, **28**. 153, 51, 520, 1926 ; C. S. Smith, *ib.*, **28**. 456, 1926 ; E. Krause, *ib.*, **29**. 534, 1926 ; A. H. Packer, *Automotive Ind.*, **53**. 831, 1925 ; W. M. Phillips, *Journ. Soc. Automotive Eng.*, **20**. 255, 1927 ; *Brit. Pat. No.* 273659, 1926 ; W. M. Phillips and P. W. C. Strausser, *ib.*, 254, 757, 1926 ; W. M. Phillips and M. F. Macaulay, *Journ. Soc. Automobile Eng.*, **24**. 397, 1929 ; G. Neuendorff, *Ueber die Schemlzflusselektrolyse von Eisen, Chrom, und Mangan*, Breslau, 1927 ; G. Neuendorff and F. Sauerwald, *Zeit. Elektrochem.*, **34**. 199, 1928 ; A. Siemens, *ib.*, **14**. 264, 1928 ; F. Adcock, *Journ. Iron Steel Inst.*, **115**. i, 369, 1927 ; D. H. Killeffer, *Journ. Ind. Eng. Chem.*, **19**. 773, 1927 ; H. S. Lukens, *Trans. Amer. Electrochem. Soc.*, **53**. 491, 1928 ; *Metal Ind.*, **32**. 567, 1908 ; *Amer. Metal Ind.*, **26**. 354, 1928 ; P. W. Ellwanger, *ib.*, **26**. 77, 1928 ; J. H. Frydlender, *Rev. Prod. Chim.*, **31**. 1, 41, 1928 ; F. Studinges, *Swiss Pat. No.* 120265, 1925 ; T. Murakami, *Journ. Japan Soc. Chem. Ind.*, **31**. 132, 1928 ; J. G. Roberts, *Journ. Glasgow Tech. Coll. Met. Club*, 6, 1927 ; J. Hausen, *Metallbörse*, **18**. 257, 314, 483, 1928 ; E. M. Baker and E. E. Pettibone, *Amer. Metal Ind.*, **26**. 520, 1928 ; *Trans. Amer. Electrochem. Soc.*, **54**. 331, 1928 ; E. M. Baker and A. M. Rente, *ib.*, **54**. 337, 1928 ; W. L. Pinner and E. M. Baker, *ib.*, **55**. 315, 1929 ; *Metal Ind.*, **34**. 585, 611, 1929 ; W. L. Pinner, *Metal Cleaning*, **1**. 249, 1929 ; G. F. K. McCullough and B. W. Gilchrist, *Brit. Pat. No.* 292094, 1927 ; H. Leiser, *Metallwaren Ind.*, **27**. 365, 1929 ; *Brit. Pat. No.* 294484, 1927 ; F. Lauterbach, *ib.*, 296988, 299395, 1927 ; M. Nagano and A. Adachi, *Bull. Research Lab. Bureau Govt.*, **19**. 23, 1928 ; J. J. Bloomfield and W. Blum, *Chem. Met. Engg.*, **36**. 351, 1929 ; O. J. Sizelove, *Amer. Metal Ind.*, **27**. 271, 1929 ; R. Justh, *Metallwaren Ind.*, **27**. 249, 1929 ; L. C. Pan, *Metal Cleaning*, **2**. 405, 1930 ; S. Dreyfus, *French Pat. No.* 673382, 1928 ; M. L. V. Gayler, *Metallwirtschaft*, **9**. 677, 1930 ; W. Obst, *Metallwaren Ind.*, **27**. 365, 389, 1929 ; P. Leistritz and F. Burghauser, *German Pat., D.R.P.* 496004, 1927 ; R. J. Piersol, *Amer. Met. Ind.*, **27**. 564, 1929 ; *U.S. Pat. No.* 1774901, 1930 ; A. Champion, *ib.*, 1753350, 1930 ; R. Blesberg, *Brit. Pat. No.* 327293, 1929 ; J. Bauer, *ib.*, 310427, 1928 ; 310876, 327911, 1929 ; V. P. Ilinsky, N. P. Lapin and L. N. Goltz, *Zhur. Prikladnoi Khim.*, **3**. 309, 1930 ; M. Ballay, *Rev. Mét.*, **27**. 316, 1930 ; *Chem. Ind.*, 253, 1930 ; A. V. Pamfiloff and G. F. Filippwicheff, *Journ. Russ. Phys. Chem. Soc.*, **61**. 22221, 1929 ; H. L. Farber and W. Blum, *Journ. Research Bur. Standards*, **4**. 27, 1930 ; D. B. Keyes and S. Swann, *Bull. Univ. Illinois Engg.*, 206, 1930 ; B. F. Lewis, *Rev. Amer. Electroplater's Soc.*, **16**. 20, 1929 ; G. Fuseya, K. Murata, and R. Yumoto, *Tech. Rep. Tohoku Univ.*, **9**. 33, 1929 ; F. Grove-Palmer, *Iron Steel Ind. Brit. Foundryman*, **2**. 401, 1929 ; L. E. Stout and J. Carol, *Journ. Ind. Eng. Chem.*, **22**. 1324, 1930 ; D. J. MacNaughtan and R. A. F. Hammond, *Trans. Faraday Soc.*, **26**. 481, 1930 ; *Journ. Electroplaters' Tech. Soc.*, **5**. 151, 1930 ;

J. W. Cuthbertson, *ib.*, **6**. 1, 1930; O. Macchia, *Ind. Chimica*, **5**. 150, 560, 1930; *Chem. News*, **141**. 1, 1930.

[3] H. Moissan, *Ann. Chim. Phys.*, (3), **21**. 199, 1880; J. Férée, *Compt. Rend.*, **121**. 822, 1895; G. Neuendorff and F. Sauerwald, *Zeit. Elektrochem.*, **34**. 199, 1926; H. Küzel, *German Pat.*, *D.R.P.* 197379, 1905; *Brit. Pat. No.* 25864, 1906; T. Svedberg, *Ber.*, **38**. 3616, 1905; **39**. 1705, 1906; *Herstellung kolloider Lösungen anorganischer Stoffe*, Dresden, 413, 1909; R. Appel, *Brit. Pat. No.* 259118, 1926; C. L. Long, D. J. Macnaughtan, and G. E. Gardam, *ib.*, 258724, 1925; F. Andersen, *Ueber die Darstellung einiger Schwermetalle und Legierungen durch Elektrolyse in Schmelzfluss*, Darmstadt, 1916; G. Bredig, *Anorganische Fermente*, Leipzig, 34, 1901; R. Taft and H. Barham, *Journ. Phys. Chem.*, **34**. 929, 1930.

§ 4. The Physical Properties of Chromium

The specimens of chromium prepared by the early investigators were more or less impure, and in some cases the impurity affected the physical properties to an appreciable extent. The metal prepared by the carbon reduction process is contaminated with carbon or carbides; and that prepared by aluminium reduction is contaminated with aluminium and silicon. Chromium prepared by heating the amalgam to about 300° is a black pyrophoric grey powder—*vide supra.* R. Bunsen[1] found that the electrolytically deposited metal to be steel-grey or silver-white. H. Moser described chromium as a steel-grey mass composed of four-sided prisms; and J. F. Gmelin obtained a metal with a dull-grey fracture and interspersed with tin-white crystals. E. Glatzel obtained chromium as a micro-crystalline, grey powder; F. Wöhler obtained it in the form of what he called grey rhombohedra; E. Jäger and G. Krüss, tin-white rhombohedra; P. A. Bolley, tetragonal pyramids; E. Frémy, and E. Zettnow, in cubic crystals; and W. Prinz said that when prepared by F. Wöhler's process, the minute cubes with pyramidal faces furnish hexagonal and octahedral contours when examined by transmitted light; and he added that the supposed rhombohedra are probably deformed octahedra. W. C. Phebus and F. C. Blake found that the **X-radiogram** agrees with a body-centred cubic lattice, with side a=2·875 A. A. W. Hull gave for the side of the elementary cube of the body-centred cubic lattice, 2·895 A.; for the distance between the nearest atoms, 2·508 A.; and for the density, 7·07; R. A. Patterson, and F. Sillers gave a=2·872 A.; E. C. Bain, a=2·899 A.; and W. C. Phebus and F. C. Blake, a=2·875 A. for the body-centred cubic lattice. W. P. Davey and T. A. Wilson, E. Schmid, R. Blix, W. Hume-Rothery, and G. F. Hüttig and F. Brodkorb made observations on this subject. H. L. Cox and I. Backhurst observed no marked effect on the X-radiograms for stresses below the elastic limit. A. J. Bradley and E. F. Ollard said that the electro-deposited chromium may exhibit **allotropy,** for it may show the hexagonal structure as well as the body-centred cubic structure. C. S. Smith observed only the latter form. The subject was discussed by F. Adcock; and H. Shoji studied the mechanism of the change of the space-lattice in passing from one allotropic form to another. A. W. Hull added that iron and chromium have a similar arrangement of atoms in the space-lattice, and this shows that ferro-magnetism does not depend on a particular arrangement of the atoms. On the other hand, A. J. Bradley and E. F. Ollard said that the X-radiogram agrees with the assumption that chromium is a mixture of two allotropes. In the predominating form, the atoms are arranged in two hexagonal lattices giving an almost hexagonal close-packed structure, the axial ratio $a:c$ being 1·625 instead of 1·633, and the distance between neighbouring atomic centres 2·714 A. and 2·70 A.

J. B. Richter gave 5·9 for the **specific gravity** of chromium; F. Wöhler, 6·81 at 25°; J. E. Loughlin, 6·2; C. F. Rammelsberg, 6·522; R. Bunsen, 6·7; E. Glatzel, 6·7179–6·737 at 16° for the crystalline powder; A. Gotta, 7·0367 to 7·0747 at 25°; H. Moissan, 6·92 at 20° for the metal previously fused in an electric furnace; A. Binet du Jassonneix, 7·1 at 17° for metal derived from the boride; and T. Döring 7·085 for 98 per cent. chromium prepared by the alumina-thermite process. K. Honda gave 6·8 for a sample with over 20 per cent. of iron. K. Ruf gave 7·014 at 20° for the pure metal, and 7·011 for electrolytic chromium. G. F. Hüttig and F. Brodkorb found that electrolytic chromium free from occluded gas had a sp. gr. of 7·138 at 25°/4°, and 7·156 at —50°/4°; hence the **atomic volume** is 7·286 at 25° and 7·268 at —50°. H. Schröder discussed the volume relations of the sulphates, selenates, and chromates; E. Donath and J. Mayrhofer, the at. vol.; and I. Traube, the at. soln. vol. E. M. Baker and A. M. Rente, and D. J. Macnaughtan discussed the porosity of electro-deposited chromium. M. L. Huggins calculated for the **atomic radius,** 1·44 A.; W. F. de Jong and H. W. V. Willems, 1·40 A. to 1·42 A.; and W. L. Bragg, 1·40 A. H. G. Grimm, V. M. Goldschmidt, L. Pauling, E. T. Wherry, J. C. Slater, and A. M. Berkenheim discussed this subject, from which it follows that for sexivalent chromium atoms, the effective at. radius is 0·52 to 0·65 A., and for typical atoms, 1·17 to 1·54 A. P. Vinassa studied the mol. number.

K. W. Schwartz said that the bluish-white metal is exceedingly hard and can be drilled only with difficulty. J. B. Dumas found that the chromium he prepared scratched glass of hardness 5·6 on Mohs' scale. H. St. C. Deville said that its **hardness** is equal to that of corundum; while H. Moissan said that it scratches glass only with difficulty; it can be polished readily and then shows a good reflecting surface. J. R. Rydberg gave 9 for its degree of hardness (diamond 10). According to F. Adcock, the great hardness of electrolytically-deposited chromium, 650 on Brinell's scale, is apparently caused by the occluded hydrogen, the crystalline form, and possibly the oxygen. It is not possessed by the metal of a high degree of purity melted or annealed at high temp. in vacuo or an atm. of hydrogen, the hardness being then as low as 70 on Brinell's scale. L. E. and L. F. Grant obtained the hardest deposits of chromium from a soln. of 209 grms. of chromic acid, 23 grms. of chromic oxide, and 6·4 grms. of chromic sulphate per litre using a current density of 33·3 amps. per sq. dm., at 45°. D. J. Macnaughtan and A. W. Hothersall gave 500 to 900 for Brinell's hardness of electro-deposited chromium; and D. J. Macnaughtan studied the porosity of the deposits. The subject was discussed by R. J. Piersol. W. Treitschke and G. Tammann found that the **viscosity** of chromium is very great when in the vicinity of the m.p. T. W. Richards found the **compressibility** of chromium, *i.e.* the mean change of vol. per megabar, between 100 and 600 megabars, to be $0\cdot7\times10^{-6}$ for 99 per cent. chromium. P. W. Bridgman found for the vol. compressibility from measurements of the linear compressibility, at 30°, $\delta v/v_0=-5\cdot187\times10^{-7}p+2\cdot19\times10^{-12}p^2$; and at 75°, $\delta v/v_0=-5\cdot310\times10^{-7}p+2\cdot19\times10^{-12}p^2$. These values are lower than the result given by T. W. Richards. W. Widder gave for the modulus of elasticity, $E=E_{20}\{1-0\cdot006536(\theta-20)\}$; M. Grube, C. J. Smithells and S. V. Williams, J. Laissus, W. van Drunen, and F. C. Kelley studied the **diffusion** of chromium with iron and nickel.

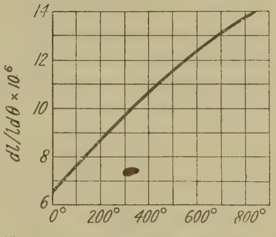


FIG. 2.—The Effect of Temperature on the Coefficient of Expansion.

J. Disch[2] found the coeff. of **thermal expansion**—linear—to be $0\cdot0_5731$ between —78° and 0°; and $0\cdot0_584$ between 0° and 100°. P. Chevenard found that the expansion curve is exactly reversible between 0° and 100° and shows no singular point. The true coeff. of expansion, 0·0000068 at 0°, increases rapidly with temp. and shows a slight concavity towards the increasing temp., Fig. 2. G. F. Hüttig and F. Brodkorb gave $1\cdot2\times10^{-5}$ for the coeff. of expansion between —50° and 25°. W. Widder gave $0\cdot0_5824$ at 20°. J. Disch gave for the linear expansion in mm. per metre:

	—78°	0°	100°	200°	300°	400°	500°
Expansion .	—0·57	0·00	0·84	0·75	2·72	3·76	4·86 mm.

E. Jäger and G. Krüss gave for the **specific heat** 0·12162 between 0° and 98·24°; H. Mache, 0·1208 between 0° and 100°; H. Schimpff 0·1044 at 0°; R. Lämmel gave 0·0898 at —100°; 0·1039 at 0°, and 0·1872 at 600°. T. W. Richards and F. G. Jackson, 0·0794 between —188° and 20°; and P. Schübel gave for the true sp. ht., c_p, and the **atomic heat**, C_p:

	50°	100°	200°	300°	400°	500°	600°
c_p .	0·1080	0·1160	0·1200	0·1211	0·1250	0·1340	0·1500
C_p .	0·63	6·05	6·25	6·30	6·50	6·99	7·81

S. Umino gave:

	100°	300°	500°	700°	900°	1100°	1300°	1500°	1640°
Sp. ht. .	0·118	0·123	0·131	0·144	0·158	0·177	0·200	0·225	0·187

F. Wüst, A. Meuthen and R. Durrer, and G. Tammann and A. Rohmann also made observations on the sp. ht. F. Michand, J. Maydel, and E. van Aubel discussed the at. ht. relations; and E. D. Eastman and co-workers, the thermal energy of the electrons in chromium, and computed $C_p—C_v=0·037$ Cal. per degree per mol. P. Nordmeyer and A. L. Bernoulli gave 0·1039 for the sp. ht. at 0°; 0·1121 at 100°; 0·1236 at 300°; 0·1503 at 500°; and 0·0860 between —185° and 20°. J. Dewar gave 0·0142 between —253° and 196° with the at. ht. 4·14. F. Simon and M. Ruhemann gave $C_p=1·249$ and $C_v=1·247$ at 71·29° K.; and $C_p=1·56$ and $C_v=1·56$ at 79·50° K. R. Lämmel represented his results by $c_p=0·103944+0·0_310591\theta—0·0_629694\theta^2+0·0_954088\theta^3$; and F. W. Adler observed:

	0°	100°	200°	300°	400°	500°	600°
c_p .	0·10394	1·11211	0·11758	0·12360	0·13343	0·15030	0·18710
C_p .	5·40	5·83	6·11	6·43	6·94	7·82	9·73

H. St. C. Deville[3] found that chromium melts at a higher temp. than is the case with manganese or platinum; and H. Moissan also stated that the **melting point** of chromium is much higher than that of platinum; for it cannot be fused by the oxyhydrogen blowpipe. E. Glatzel, however, fused it by the oxyhydrogen flame. S. O. Cowper-Cowles gave 2000° for the m.p.; but this is too high. E. A. Lewis found that the metal made by the aluminium-thermite process melted at 1515°±5°. G. K. Burgess gave for 99 per cent. chromium, 1489°; E. Tiede and E. Birnbräuer, 1420°; E. Newbery and J. N. Pring, 1615°±15°; W. Treitschke and G. Tammann, 1513°; S. Umino, 1600° (95·39 per cent. Cr); R. S. Williams, and G. Voss, 1553°; K. Lewkonja, 1547°; J. Johnston, 1510°; G. Hindrichs, 1550°; and R. Vogel and E. Trilling give 1575°. K. Honda gave 1515° for a sample with about 20 per cent. of iron. W. Guertler and M. Pirini, W. R. Mott, and G. K. Burgess and R. G. Waltenberg gave for the best representative value 1520°; but L. I. Dana and P. D. Foote gave 1615°. A. von Vogesack said that the m.p. of chromium is over 1700°, and that the lower values are due to the presence of carbon obtained from the carbon monoxide in the atmosphere in which the metal is melted; whilst with C. J. Smithells and S. V. Williams, 1920° was thought to be a low value for the m.p. H. Moissan said that when chromium is fused in the electric arc-furnace it forms a very fluid, bright liquid with the appearance and fluidity of mercury; and it can be cast in a mould. It can be distilled in the electric arc-furnace; and H. C. Greenwood gave 2200° for the **boiling point** of chromium—W. R. Mott estimated 3000°. J. Johnston gave for the **vapour pressure** $\log p=—14900T^{-1}+8·91$; and

	980°	1090°	1230°	1400°	1610°	1800°	1890°	2200°
p .	10^{-3}	10^{-2}	10^{-1}	1	10	50	100	760

F. Wüst and co-workers, and W. Herz gave 32·00 Cals. for the latent **heat of fusion** per gram; and S. Umino, 70·05 Cals. E. Kordes gave 0·91 (cals.) for the entropy of chromium. G. N. Lewis and co-workers gave 5·8 for the at. **entropy** of chromium at 25°; W. Herz, 10·85; and B. Bruzs, 19·8 at the m.p. E. D. Eastman and co-workers studied this subject; and R. D. Kleeman, the internal and free energy of chromium.

A. L. Bernoulli[4] gave 2·67 for the **index of refraction** of chromium, and 1·63 for the absorption coeff. for Na-light. H. von Wartenberg gave 2·97 for the index of refraction, μ; 4·85 for the absorption coeff., k; and 69·7 per cent. for the **reflecting power,** R. V. Fréedericksz gave

λ	257$\mu\mu$	325$\mu\mu$	361$\mu\mu$	444$\mu\mu$	502$\mu\mu$	668$\mu\mu$
μ	1·641	1·259	1·530	2·363	2·928	3·281
k	3·69	2·91	3·21	4·44	4·55	4·30

W. W. Coblentz and R. Stair, and W. W. Coblentz gave for the **reflecting power**

λ	0·5μ	1·0μ	2·0μ	3·0μ	4·0μ	5·0μ	9·0μ
R	55	57	63	70	76	81	92 per cent.

P. R. Gleason, W. W. Coblentz and R. Stair, and M. Luckiesh made observations on the subject. V. Fréedericksz gave 60 to 72 per cent. for λ=257$\mu\mu$ to 668$\mu\mu$. F. J. Michéli observed no difference between the reflecting power of passive and active chromium, although in the case of passive and active iron, the results indicated that a film was formed. A. L. Bernoulli found that the results of F. J. Michéli were anomalous owing to gas absorption, for there is a marked difference in the reflecting powers of the active and passive forms of chromium—this is attributed to the presence of a surface film on the passive metal. J. H. Gladstone found the **refraction equivalent** of chromium to be 15·9; and the **specific refraction,** 0·305. W. J. Pope gave 22·25 for the refraction eq. of tervalent chromium. T. Bayley,[5] and M. N. Saha discussed the colour relations of chromium and of copper, manganese, iron, cobalt, and nickel; and J. Piccard and E. Thomas, of chromous and chromic ions, and of chromates and dichromates. W. Biltz discussed the relation between colour and the magnetic properties of the element.

Chromium compounds do not give the ordinary **flame spectrum.** V. Merz[6] said that when a chromate moistened with sulphuric acid is introduced at the edge of the colourless gas flame, the edge of the flame acquires a dark reddish-brown colour and a rose-red mantle which can be recognized with 0·001 mgrm. of the chromate. K. Someya observed that the colourless soln. obtained by reducing a very dil. soln. of potassium dichromate shows that chromous ions are colourless, and that thiocyanate produces the blue colour of conc. soln. owing to the formation of complex ions. F. Gottschalk and E. Drechsel found that the vapour of chromyl chloride in the oxy-coal gas flame shows a band spectrum in the green and yellow. A. Gouy found that when chromium salts are fed into the bunsen flame, the inner cone shows some spectral lines. J. N. Lockyer also found spectral bands with chromium salts in the oxy-coal gas flame, and G. D. Liveing and J. Dewar observed numerous lines in the specimen of the explosion flame of electrolytic gas with chromium salts. W. N. Hartley observed the oxy-hydrogen flame spectrum. H. W. Vogel, M. A. Catalan, and C. de Watteville studied this subject. G. Kirchhoff first investigated the **spark spectrum,** and he was followed by W. A. Miller, W. Huggins, R. Thalén, C. C. Kiess, A. Mitscherlich, L. de Boisbaudran, G. Ciamician, J. Parry and A. E. Tucker, G. D. Liveing and J. Dewar, J. N. Lockyer, F. McClean, E. Demarçay, L. and E. Bloch, A. de Gramont, W. E. Adeney, R. J. Lang, O. Lohse, F. Exner and E. Haschek, R. E. Loving, A. Hagenbach and H. Konen, M. A. Catalan, J. H. Pollock, J. H. Pollock and A. G. G. Leonhard, F. L. Cooper, J. M. Eder and E. Valenta, and H. Smith. The simple spark spectrum shown by, say, a soln. of chromic chloride is characteristic, and can be employed in the spectroscopic detection of chromium, Fig. 3. There is the 5207-line in the green; and a group of three

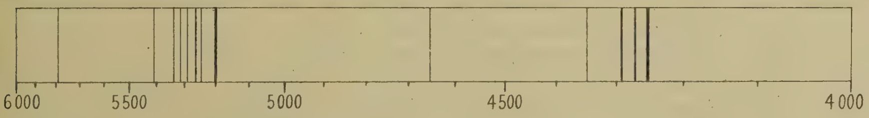


FIG. 3.—Spark Spectrum of Chromium.

lines 4290, 4275, and 4254 in the indigo-blue, which are well defined, while there are feebler lines 4345 in the blue; 5253, 5276, 5297, 5341, and 5410 in the green; and 5790 in the orange-yellow. E. O. Hulburt studied the spectrum of the condensed spark in aq. soln. The **arc spectrum** of chromium was studied by J. N. Lockyer, B. Hasselberg, F. Exner and E. Haschek, M. A. Catalan, H. Gieseler, Lord Blythwood and W. A. Scoble, R. Frerichs, A. S. King, A. B. McLay, J. Clodius, D. Foster, L. Stüting, K. Burns, S. P. de Rubies, J. Buchholz, C. C. Kiess, C. C. Kiess and W. F. Meggers, and J. Hall. The **ultra-violet spectrum** was studied by W. A. Miller, J. C. McLennan, A. B. McLay, R. A. Millikan and I. S. Bowen, V. Schumann, F. Exner and E. Haschek, L. and E. Bloch, W. E. Adeney, M. Edlen and M. Ericson, and R. Richter; the **ultra-red spectrum,** by K. W. Meissner, T. Dreisch, and H. M. Randall and E. F. Barker. H. Finger examined the effect of the *medium* on the lines in the spark spectrum; F. Croze, M. A. Catalan, and A. de Gramont, *les raies ultimes*, and *les raies de grand sensibilité;* G. D. Liveing and J. Dewar, the *reversed lines* in metal vapours; J. N. Lockyer and F. E. Baxandall, M. Kimura and G. Nakamura, and J. N. Lockyer, the *enhanced lines;* A. S. King, and H. Geieler, the *anomalous dispersion;* W. J. Humphreys, the effect of *pressure;* J. A. Anderson, and H. Nagaoka and Y. Sugiura, the **Stark effect** or the influence of an *electric field* on the arc spectrum; and A. Dufour, H. du Bois and G. J. Elias, W. Miller, J. E. Purvis, C. Wali-Mohammad, O. Lüttig, W. C. van Geel, E. Krömer, and W. Hartmann, the **Zeeman effect.** The **absorption spectrum** of the vapour was examined by J. N. Lockyer and W. C. Roberts-Austen, R. V. Zumstein, H. D. Babcock, A. S. King, A. W. Smith and M. Muskat, H. Gieseler and W. Grotrian, and W. Gerlach; the absorption spectrum of aq. soln. of various salts (*q.v.*) was examined by W. de W. Abney and E. R. Festing, W. Ackroyd, T. Bayley, H. Becquerel, W. Böhlendorff, H. Bremer, D. Brewster, A. Byk and H. Jaffe, T. Carnelley, S. Kato, H. Croft, T. Erhard, A. Étard, J. Formanek, J. Gay, J. H. Gladstone, F. Hamburger, A. Hantzsch, A. Hantzsch and R. H. Clark, W. N. Hartley, J. M. Hiebendaal, H. C. Jones and W. W. Strong, G. Joos, B. Käbitz, O. Knoblanch, W. Lapraik, H. Fromherz, G. D. Liveing and J. Dewar, G. Magnanini, G. Magnanini and T. Bentivoglio, F. Melde, W. A. Miller, H. Moissan, J. Müller, E. L. Nichols, C. Pulfrich, A. Recoura, G. B. Rizzo, P. Sabatier, C. A. Schunck, H. Settegast, C. P. Smyth, J. L. Soret, G. J. Stoney and J. E. Reynolds, H. F. Talbot, H. M. Vernon, K. Vierordt, E. Viterbi and G. Krausz, H. W. Vogel, E. Wiedemann, and C. Zimmermann; and the absorption lines in the spark spectrum under water, by E. O. Hulburt. J. Formanek said that the chromium salts do not react with alkanna tincture. L. de Boisbaudran examined the **fluorescence spectrum.** According to T. Tanaka, chromium is the principal agent in the cathodoluminescence of corundum. No **series spectrum** has been observed with chromium, but the lines have been studied from this point of view by L. Janicki, A. Dufour, P. G. Nutting, H. N. Russell, S. Goudsmit, E. Krömer, M. Steenbeck, H. Deslandres, A. Sommerfeld, H. E. White, H. E. White and R. C. Gibbs, M. A. Catalan, R. Mecke, H. Gieseler, R. Frerichs, R. J. Lang, C. V. Ramon and S. K. Datta, G. Wentzel, Y. M. Woo, C. Wali-Mohammed, H. Pickhan, C. C. and H. Kiess, A. de Gramont, O. Laporte, W. F. Meggers and co-workers, A. E. Ruark and R. L. Chenault, C. C. Kiess and O. Laporte, R. J. Lang, M. A. Catalan, C. E. Hesthal, and N. Seljakoff and A. Krasnikoff.

B. Rosen,[7] M. Levi, and G. Kettmann studied the **X-ray spectrum**. The K-series in the X-ray spectrum was studied by V. Dolejsek, V. Dolejsek and K. Pestrecoff, B. C. Mukherjee and B. B. Ray, M. Steenbeck, C. G. J. Moseley, W. Duane and co-workers, D. Coster, G. Wentzel, N. Selijakoff and A. Krasnikoff, E. C. Unnewehr, A. E. Lindh, H. Fricke, S. Eriksson, T. L. de Bruin, W. Bothe, B. Kievit and G. A. Lindsay, F. Wisshak, S. Pastorello, J. H. van Vleck and A. Frank, H. Beuthe, H. R. Robinson and C. L. Young, N. Seljakoff and co-workers, M. J. Druyvesteyn, R. C. Gibbs and H. E. White, F. Hjalmar, K. Chamberlain, O. Stelling, M. Siegbahn and co-workers, B. Walter, J. Schrör, and H. Stensson. There are the lines $\alpha_2\alpha'=2{\cdot}28855$; $\alpha_1\alpha=2{\cdot}28517$; $\alpha_3\alpha_4=2{\cdot}2733$; $\beta_1\beta=2{\cdot}08144$; and $\beta_2\gamma=2{\cdot}069$. The L-series was examined by J. Schrör, A. Duvanlier, C. E. Howe, F. de Boer, F. P. Mulder, G. Kellström, F. L. Hunt, and R. Thoroeus; the M-series, by F. P. Mulder, and B. C. Mukherjee and B. B. Ray; the N-series, by F. P. Mulder; and the O-series, by F. P. Mulder.

U. Andrewes and co-workers [8] studied the absorption of **X-rays.** The absorption coefficients of X-rays from chromium radiator were studied by U. Andrewes and co-workers, D. M. Bose, C. G. Barkla and C. A. Sadler, and T. E. Aurén. O. W. Richardson and F. S. Robertson investigated the soft X-rays from chromium. A. C. Davies and F. Horton gave the critical potentials for soft X-rays. J. C. McLennan, and M. A. Catalan gave 6·7 volts for the **ionization potential,** and 2·89 volts for the first **resonance potential.** H. N. Russell gave 6·74 volts for the first ionization potential and 16·6 volts for the second. B. B. Ray and R. C. Mazumdar discussed the critical potential; E. Rupp, the deflection of electrons by films of chromium; and R. H. Ghosh, and B. B. Ray and R. C. Mazumdar, the relation between the ionizing potential and the electronic structure. E. Rabinowitsch and E. Thilo studied the subject. J. E. P. Wagstaff gave $8{\cdot}3\times10^{12}$ for the **vibration frequency;** and W. Herz, $8{\cdot}43\times10^{12}$. According to R. Whiddington, the critical velocities of cathode rays required to excite K- and L-radiations with the chromium radiator are respectively $5{\cdot}0\times10^9$ and $2{\cdot}0\times10^8$ cm. per sec. E. C. Unnewehr studied the dependence of the energy of emission of the K-radiation on the applied voltage. The use of chromium as a radiator for X-rays was discussed by R. Whiddington, and C. A. Sadler and A. J. Steven. A. Wehnelt classed chromic oxide as an "inactive oxide" so far as the emission of electrons is concerned, when it is fixed on a platinum disc and used as a cathode of a discharge tube; but A. Poirot found that **anode rays** are emitted from chromium. W. Espe studied the subject. E. Rupp discussed the passage of electrons through thin films of chromium. P. Weiss and G. Foex calculated values for the **atomic moments;** O. W. Richardson and F. S. Robertson studied the **photoelectric effect,** and U. Nakaya examined the influence of adsorbed gas on this phenomenon. R. E. Nyswander and B. E. Cohn studied the thermoluminescence of glass activated with chromium.

P. E. Shaw and C. S. Jex [9] said that chromium acquires negative **triboelectricity** when rubbed on glass. K. F. Herzfeld discussed the metallic conductivity of chromium. I. I. Shukoff gave $38{\cdot}5\times10$ mhos for the **electrical conductivity** of chromium at 0°; and A. Schulze gave $2{\cdot}60\times10^{-6}$ for the sp. resistance at 0°. J. C. McLennan and C. D. Niven gave for the sp. resistance, R, of aged and unaged chromium:

		29°	27°	−152·4°	−193°	−190°	−268·8°	−269·99°	−270·8°
R	aged .	17·2	—	0·90	2·01	—	—	—	—
	unaged .	—	43·8	27·0	—	28·8	26·7	26·6	26·5

They observed no indication of superconductivity at low temp. P. W. Bridgman gave $-5{\cdot}8\times10^{-7}$ for the press. coeff. of the resistance; and 0·000033 for the temp. coeff., the resistance at 30° being 160×10^5. The values are taken to represent an impure metal. J. C. McLennan and co-workers found for the resistance of aged chromium, at different temp. absolute, to be:

	292°	273°	80°	20·6°	4·2°	2·25° K.
$R\times10^3$ . .	5·59	—	0·655	0·260	0·258	0·258 ohms
Sp. resistance .	17·2	15·25	2·01	0·80	0·79	0·79

The values of the ratio R/R_0 at liquid air temp. is 0·132, and at liquid hydrogen temp., 0·059. P. Kapitza examined the effect of a magnetic field on the electrical conductivity. Z. A. Epstein compared the electrical conductivities of the elements and their position in the periodic table. K. Hopfgartner found that the transport numbers of the chromic ion in hydrochloric acid soln., are 0·318, 0·357, and 0·414 respectively for 1·00, 0·32, and 0·075 eq. soln.—*i.e.* for zero concentration, 0·446.

The mobility of the chromic ion is 46·3 to 53. It is assumed that the chromic ion is surrounded by a fairly large water-sheath. E. Newbery discussed the over-voltage; S. J. French and L. Kahlenberg, the gas-metal electrodes obtained by chromium and oxygen, nitrogen, or hydrogen; and N. Koboseff and N. I. Nebrassoff, the cathodic polarization.

According to J. J. Berzelius, there are two allotropic forms of chromium. The one, α-**chromium,** obtained as a grey metallic powder by reducing chromium trichloride with potassium, inflames between 200° and 300° and burns vividly to chromic oxide, and it dissolves readily in hydrochloric acid with the evolution of hydrogen; the other, β-**chromium,** obtained by reduction with carbon at a high temp., cannot be oxidized by heat, by boiling with aqua regia, by hydrofluoric acid, or by ignition with potassium hydroxide or nitrate. He added that corresponding modifications can be traced through many of the compounds of chromium; but this statement is not now regarded as correct because certain allotropic forms of the salt are now explained without assuming that they are due to allotropic forms of the element. As indicated above, R. Bunsen asked if the electrolysis of soln. of the green and violet chromium salts would give corresponding allotropic forms of the element, but the answer is in the negative. W. Hittorf recognized that chromium can exist in an active and in a **passive state.** Chromium is active in contact with hydrofluoric, hydrochloric, hydrobromic, hydriodic, acetic, oxalic, sulphuric, and hydrofluosilicic acids, that is, the metal dissolves in these acids with the evolution of hydrogen, if the acids are concentrated and cold, and if the acids are dilute, application of heat may be required. On the other hand, chromium is passive in chlorine or bromine water, in conc. nitric, chromic, phosphoric, chloric, perchloric, citric, formic, or tartaric acid, for the metal does not dissolve therein. The difference in its behaviour towards these acids is associated with a difference in the electrode potential of chromium for the difference in the e.m.f. of the two states amounts to about 1·6 volts, for with active chromium, the e.m.f. of the cell Cr/acid, H_2CrO_4/Pt is about 1·9 volt, and with the passive metal, 0·3 volt. In the electrochemical series, active chromium is close to zinc, but passive chromium stands near platinum. Otherwise expressed, passive chromium behaves as a noble metal, being electronegative towards zinc, cadmium, iron, nickel, copper, mercury, and silver, for it does not decompose even boiling soln. of these salts, excepting that it reduces mercuric and cupric salts respectively to mercurous and cuprous salts. When chromium is employed as anode in soln. in which it is indifferent, it becomes covered with a yellow film of chromic acid, and the loss of weight of the anode was found to correspond with the production of sexivalent chromium ions; this occurs even in soln. of hydrogen chloride in which chromium ordinarily dissolves with the formation of chromous salts. This may be due either to the decomposition of the water by the anion and subsequent formation of chromic acid from the liberated oxygen, or to the formation of a compound of sexivalent chromium with the anion and the decomposition of this compound by water; no such compound, however, is actually known to exist. In soln. of potassium thiocyanate or of an iodide, the chromium anode experiences no loss. The coeff. of the amalgamated metal M in the cell M | KCl, $NaNO_3$, $AgNO_3$ | Ag at 5° are:

M .	Zn	Cd	Pt	Fe	Sn	Cu	Cr
Volt .	1·534	0·974	1·123	0·955	1·010	0·689	0

W. J. Müller found that there are certain current densities which vary with the time required to make the metal passive. W. Muthmann and F. Fraunberger found the electrode potential between chromium and N-KCl against the normal calomel electrode zero to be $-0·63$ volt for the most active metal, and $+1·19$ volt for the most passive. Fresh electrolytic chromium was found by B. Neumann to be strongly active. W. Muthmann and F. Fraunberger observed variations of the electrode potential with the same piece of metal. A piece 25 cms. long had a potential of $-0·03$ volt at one end, and $+0·03$ at the other; and when activated,

—0·17 volt and —0·07 volt. W. Rathert observed that a piece of chromium polished in air had a potential against 0·1N-H_2SO_4 of +0·26 volt, and after lying some time in air, +0·37 volt; and when polished, in hydrogen, —0·054 volt at first, and +0·071 after standing 3 minutes in the liquid. Thus, polished chromium is not active in hydrogen. Passive chromium becomes active when it is charged electrolytically with hydrogen; but molecular hydrogen has scarcely any action on the potential of a passive chromium electrode. A. M. Hasebrink observed that when chromium is treated with nitric acid, and heated in nitrogen, it remains active a few hours, and then becomes passive; if hydrochloric acid be substituted for nitric acid, the chromium remains active as long as it is kept in nitrogen. Chromium activated in hydrogen remains active in this gas. At ordinary temp., nitrogen, hydrogen, and carbon dioxide do not activate chromium, nor do they passivate chromium made active by scratching. Occluded gases influence the rate of activation or passivation of chromium. Oxygen favours passivation, hydrogen retards it. Atm. oxygen rapidly passivates chromium; iodine acts as an activating agent, never as a passivating agent. The potential of chromium or nickel rubbed with emery in an indifferent atm., falls at first, then recovers partially; and after repeated rubbings, a constant potential is finally reached which is lower than the initial one. Molecular oxygen passed through an electrolyte, during the electrolysis of chromium, raises its potential; but the potential is scarcely affected if hydrogen or nitrogen be employed in place of oxygen. Electrolytic oxygen or hydrogen affect the potential enormously. The subject was discussed by T. Murakami, and B. Strauss and J. Hinnüber.

As previously indicated, chromium becomes passive when treated with certain oxidizing agents—*e.g.* chlorine or bromine-water, soln. of iodine and potassium iodide, conc. nitric and chromic acids, chloric acid, potassium permanganate, potassium ferricyanide, ferric chloride, and oxygen or air—N. Isgarischeff and A. Obrutscheva also found that oxidizing agents—like chromic acid, hydrogen dioxide, potassium permanganate—and exposure to air or to electrolytic oxygen make the metal passive; and, according to A. L. Bernoulli, the action of a soln. of quinine in benzene. Chromium also becomes passive when used as anode in an electrolytic cell. J. Alvarez found the strength of the current necessary to produce the passive state—the *critical strength of current*—depends on the conc. and temp. of the electrolyte. Thus, with 2·8N-, 0·7N-, and 0·175N-HCl, the critical voltages were 0·35, 0·085, and 0·034 volt respectively; and with 5N-, 0·6N-, and 0·075N-H_2SO_4, respectively 0·098, 0·046, and 0·018 volt. C. Fredenhagen applied a gradually increasing or decreasing e.m.f. to a chromium electrode immersed in sulphuric acid, and determined the electrode potential and the strength of the polarization current. The electrode potential at the point where activity or passivity sets in is not well-defined, and this is taken to support the hypothesis that passivity does not depend on the formation of an oxide film or of another modification of the metal, but is rather related to the rate at which the metal becomes charged with oxygen. The electrode potential attained when passivity or activity sets in is very sensitive to slight changes in the conc. of the acid; and a rise of temp. favours the active state. The passive condition is said to be attained when the oxygen polarization extends uniformly over the whole surface of the electrode; and the appearance of the active state when the polarization e.m.f. is lowered is due to the fact that the reactions which use up oxygen begin to overbalance those which produce oxygen. According to W. Rathert, the potential at which the passive metal becomes active is not the same as that at which the active metal becomes passive, and that the abrupt change observed by F. Flade does not represent a boundary potential below which the metal is active and above which it is passive. The metal may be active or passive on both sides of this point depending on its previous treatment. U. Sborgi and G. Cappon found that chromium in an ethyl alcohol soln. of calcium nitrate and ammonium nitrate is passive with low-current densities, and with high-current densities chromium salts are formed. E. Becker and H. Hilberg found that the maximum distance for establishing contact with a metal surface is slightly greater for passive than for active chromium.

According to W. Hittorf, and A. Meyer, and as indicated above, passive chromium is activated by soln. of hydrofluoric acid and of a number of other acids—*e.g.* hydrochloric, hydrobromic, hydriodic, sulphuric, and oxalic acids—by the halogens, and by raising the temp. The more dil. the acid, the higher the temp. necessary for activation; hydrogen is evolved, and chromous salts are formed. Soln. of the chlorides of the alkaline and alkaline earths act at a higher temp.; soln. of potassium bromide, cupric chloride or palladium dichloride do not act at 100°. The molten fluorides, chlorides, bromides, and iodides are good activating agents, and A. L. Bernoulli observed that chromium is activated when heated with benzene, toluene, naphthalene, and anthracene; and, according to N. Isgarischeff and A. Obrutscheva, when the surface is mechanically purified. The metal is activated by using it as cathode with indifferent acids like formic, citric, or phosphoric, *i.e.* by electrolytic reduction. The current required is greater the more dil. the soln., and the lower the temp. According to G. C. Schmidt, passive chromium becomes active by disturbing the surface, by scratching, knocking, and so on, but in nitric acid it remains permanently passive. Activated chromium placed in dil. hydrochloric or sulphuric acid remains permanently active. On removal from the acid, however, it becomes passive again after a short time, even although oxygen is rigorously kept away. Chromium heated in a vacuum or in nitrogen is active. In hydrochloric acid at 100° it is also active, and at this temp. chlorine, bromine, and iodine attack chromium and activate it, solely because the surface is disturbed. H. Eggert observed that chromium remains active in dry hydrogen, or nitrogen, but becomes passive if oxygen be present or if it be exposed to air. W. Rathert found that passive chromium becomes active when it has absorbed hydrogen ions by diffusion, and it then dissolves electrolytically in accord with Faraday's law. U. Sborgi and A. Borgia observed that a magnetic field had no influence.

Active chromium is indifferent towards water, but in strong acids it dissolves forming chromous salts, and in weak acids it dissolves when it is the cathode in an electrolytic cell, producing chromous salts: $Cr+2HCl=CrCl_2+H_2$. The dissolution of a chromium anode to form bivalent chromium ions is then in accord with Faraday's law so that $1Ag=\frac{1}{2}Cr$. The highest numerical value for the electrode potential observed by W. Muthmann and F. Fraunberger is —0·63 volt with N-KCl; B. Neumann observed —0·535 volt with chromic sulphate; —0·518 volt with chromic chloride; and —0·516 volt with chromic acetate; and W. Rathert obtained with N-$Cr_2(SO_4)_3$, —0·395 volt, and with 0·1N-H_2SO_4, —0·491 volt. The potential of the active metal towards normal soln. of $Cr^{\cdot\cdot}$-ions is —0·6 volt. N. Bouman gave —0·546 volt for chromium in N-H_2SO_4. This potential is independent of the metal on which the chromium is deposited, and also of the method of activation. It is also independent of the ratio of $Cr^{\cdot\cdot}$- to $Cr^{\cdot\cdot\cdot}$-ions in soln. It is curious that, with increasing hydrogen-ion concentration, the potential becomes more positive in sulphuric acid, but more negative in hydrochloric acid soln. Chromium remains active only when the acidity is above a certain limit, about 0·001N. A. H. W. Aten gave —0·75 volt, or, when referred to the hydrogen electrode, —0·47 volt. This active potential is attained only when sufficient hydrogen is present; hydrogen hastens the attainment of the electrode equilibrium. Active chromium can be anodically polarized in a soln. of potassium chloride without becoming passive. If the metal immersed in a soln. of chromous sulphate is anodically polarized with a sufficiently strong current, the chromium becomes passive, but when the current is interrupted, the potential of the metal is found to be more negative than before polarization. The passivation during anodic polarization and activation after this treatment are shown by chromium which has been deposited on copper, silver, or gold. The degree of activation after anodic polarization increases with the strength of the polarizing current. The resistance offered by the metal to the action of the polarizing current is greater when the strength of the current is gradually increased than when the current strength is increased rapidly. The resisting power of the metal is smaller when the chromium has been previously subjected to cathodic polarization. Active chromium reduces fused cadmium chloride, bromide, or iodide, and the chlorides of copper, silver, and lead ; as well as hot soln. of copper, gold, palladium, and platinum, and it thereby becomes passive. Passive chromium, as indicated above, differs from active chromium in that it is covered with a surface film of some kind, and it then behaves like a noble metal, for it does not dissolve in nitric, chloric, or perchloric acid ; it is indifferent towards neutral soln. of the salts of copper, silver, cadmium, mercury, and nickel—*vide supra* ; and it does not reduce soln. of the chlorides of gold, palladium, or platinum. It then appears to be a nobler metal than copper, silver, or mercury. The presence or absence of a film was discussed by W. J. Müller, and J. Hinnüber. W. Muthmann and F. Fraunberger observed that the electrode potential in N-KCl may be as great as +1·19 volt. N. Bouman found that in the passive state, the potential of chromium in potassium chloride soln. depends on the previous treatment which it has received, and this is shown to be equally true of other metals, including platinum. Consequently, no conclusions can be drawn from such measurements relative to the state of the metal. The potential of passive chromium varies with the metal on which it is deposited. When chromium is polarized anodically, the potential varies in the same way with the acidity as the potential of the unattackable electrode. The polarization tension is therefore governed by the reaction $Cr^{\cdots}+3H_2O=CrO_3+6H^{\cdot}+3(+)$. When passive chromium dissolves at the anode it forms chromic acid, and the dissolution is in accord with Faraday's law provided $1Ag=\frac{1}{6}Cr$. Otherwise expressed, passive chromium dissolves as sexivalent chromium ions. R. Luther said that the anode potential is +0·6 volt and energy is required for the reaction symbolized : $Cr+4H_2O\rightarrow H_2CrO_4+3H_2O$, or $Cr+4H_2O+6(+)\rightarrow CrO_4''+8H^{\cdot}$. The active and passive states are mutually convertible one into the other by a suitable change in the conditions. Thus, W. Rathert found that with active chromium dipping in N-$Cr_2(SO_4)_3$, the electrode potential at the beginning was —0·395 volt, and in 2, 23, and 73 min. was respectively —0·359, —0·209, and —0·129 volt ; and E. Grave found that passive chromium in 0·1N-KOH had an electrode potential of +1·895 volt at the beginning, after 20 sec. +1·176 volt, and after 1, 5, and 12 min. respectively +1·084, +0·981, and +0·925 volt. A. L. Bernoulli found that passive chromium is activated by aromatic hydrocarbons —benzene, toluene, *p*-xylene, naphthalene, and anthracene—and the changes in the e.m.f. are greater the more readily the hydrocarbon is oxidized. Active chromium becomes passive when treated with a boiling soln. of *p*-benzoquinone in benzene ; and also by exposure to air. According to A. H. W. Aten, if chromium has been rendered passive by anodic polarization, in a soln. of potassium chloride, the active condition may be restored by heating the soln. This change occurs even when the polarizing current is continued during the heating of the soln. and on cooling, the chromium remains in the active condition, provided the current is not too strong. U. Sborgi and G. Cappon found that in an alcoholic soln. of calcium or ammonium nitrate, chromium shows passivity phenomena similar to those which occur in aq. soln.

W. Hittorf concluded that the passivity of chromium is not due to the formation of an oxide film, but rather to the metal assuming a different electrical state ; the metal in the passive state is in a strained or coerced condition—*Zwangzustand*—so that instead of dissolving as a bivalent element it dissolves as a sexivalent element. The film hypothesis, discussed in connection with the passivity of iron, best fits the facts. C. W. Bennett and W. S. Burnham stated that the film is best regarded as a film of oxide which is rendered stable by adsorption into the metal. The oxide is usually unstable, but becomes stable when adsorbed by the metal. The oxide is not higher than CrO_3, and is probably $Cr(CrO_4)$, or CrO_2, but in the further oxidation at the anode, the higher oxide CrO_3 is formed, and the chromium passes into soln. in the sexivalent state. A. L. Bernoulli gave Cr_5O_9, or $2Cr_2O_3.CrO_3$, for the composition of the film. The subject has been discussed by A. Adler, F. Flade, C. Fredenhagen, E. Grave, W. J. Müller and co-workers, W. Rathert, O. Sackur, H. Kuessner, E. Newbery, G. C. Schmidt, etc.—*vide* iron. N. Bouman favoured the allotropic theory. According to N. Isgarischeff and A. Obrutscheva, chromium shows no definite transition point at which it passes into the active state; the metal can become active at any temp.; the activation depends on the properties of the medium. This and the mode of formation of passive chromium show that the passivity of chromium is connected with the formation of a protecting oxide film on the surface. The protecting film is a transparent, colloidal substance, the density and permanence, and consequently the passivating action, of which depend on the nature of the medium, particularly on the presence of those ions, such as chloride- and bromide-ions, which bring about colloidal transitions. Chloride-ions have the greatest disturbing effect on the film, and make it permeable to most reagents. Particles of passive chromium become active when brought into contact with active chromium zinc, or magnesium. Since these metals are all more electro-negative than passive chromium, this action is due to the formation of a galvanic element which liberates hydrogen and consequently reduces the oxide film. The oxide film is also the cause of the anomalies of chromium. E. Liebreich and W. Wiederholt plotted the current density against the potential of electrolytic chromium in $1{\cdot}02N$-K_2SO_4. At high current densities, the chromium dissolves as chromate, at lower current densities and potentials, Fig. 4, the metal acquires a film of the chromic chromate and dissolves only slightly at a potential of about 0·5 volt, and a small current density, the potential gives a slight rise with falling current density and true passivity, owing to the insolubility of a film of hydroxide, sets in. The passivity persists when the metal is made a cathode at small current densities. The curve for a potential of 0·4 volt rises steeply as the metal dissolves to form chromous salts which are partially oxidized near the electrode forming secondary hydrogen: $2CrSO_4+H_2SO_4=Cr_2(SO_4)_3+H_2$. At higher current densities, and at about $-0{\cdot}5$ volt, the metal dissolves forming hydrogen directly. G. Grube and co-workers found that with an active chromium electrode (prepared by cathodic polarization) with $0{\cdot}02$–$0{\cdot}2N$-sulphuric and hydrochloric acid soln., the anode potential is found to increase suddenly when the anode current density reaches a certain value. This critical value increases with the conc. of the acid and with increasing temp. During the first stage, the chromium ions pass into soln. entirely in the bivalent condition, and, during the second stage, entirely in the sexivalent condition. At the ordinary temp., N-NaCl behaves similarly, but at higher temp. the current density-potential curves are of somewhat different form. H. Kuessner suggested that it is possible for chromium ions of varying valency to be formed simultaneously in soln. G. Grube and co-workers hold that chromium goes primarily into soln. as bivalent ions at lower current densities, and that these are immediately oxidized to the tervalent condition, whilst at higher current densities sexivalent ions are formed. The anode potential in N-, $4N$-, $8N$-, and $16N$-potassium hydroxide soln. has also been studied at different temp.; for low current densities, the curve is discontinuous as in acid soln., and a similar explanation is adopted. In the alkaline soln., the anode becomes coated with a fine grey powder, which apparently consists

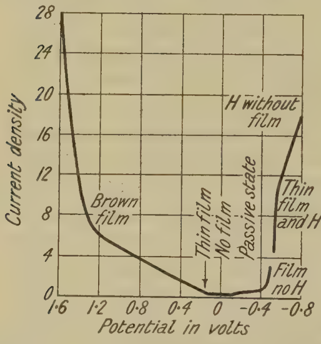


FIG. 4.—Current Density-Potential Curves of Chromium.

of a lower oxide of chromium. The facts support the oxide film theory of passivity. F. Krüger and E. Nähring found the X-radiograms of active and passive metal support the oxide-film theory. The subject was discussed by U. R. Evans. A. M. Hasebrink's chemical experiments favour the oxide film theory, but not the hydrogen theory, or the surface-tension theory of W. Hittorf, and G. C. Schmidt. L. McCulloch found cases of passivity with sparingly-soluble sulphate films.

A. S. Russell supposed that when in the active state, the atoms of chromium have two electrons in the fourth quantum orbit, and that when the metal becomes passive one of these electrons is removed to the third quantum orbit. The subject was studied by E. Müller, E. Liebreich, H. Eggert, and N. Isgarischeff and A. Obrutscheva. W. J. Müller and E. Noack found that with thermite chromium in N-H_2SO_4, so long as the current density falls below a certain critical value, i_c, which varied from sample to sample according to treatment, the metal remained active, and dissolved with the evolution of hydrogen. On exceeding this critical value, a fall of density immediately set in, during which the log of the density varied inversely as the time since the commencement of the fall, and after sufficient time complete passivity resulted. Log i_c was inversely proportional to the temp. between 0° and 35°. The activity of the chromium was characterized by a potential of $-0{\cdot}34$ volt, and passivity by zero potential, so that during the time of falling density, the metal remained active. In W. J. Müller's theory of the passivity of iron, the metal dissolves in the acid, but owing to the high mobility of the hydrogen ions, the anodic soln. becomes impoverished in these; hence basic ferrous salt is formed and deposits on the electrode when the soln. becomes saturated, thus increasing the resistance and decreasing the current, causing complete passivity only when the covering is complete. With chromium, the chromous salt first formed by dissolution of the metal in the acid rapidly oxidizes to chromic salt (hydrogen being evolved), which hydrolyzes much more rapidly than the iron salts; with high current densities (*e.g.* 1400 milliamp. per sq. cm.), the time required for passivity is only 0·3 sec. With perfectly clean metal the fall of current density is often suspended for a time and then occurs suddenly; this is explained by the supersaturation of the soln. with regard to hydroxide, which would be possible only in the absence of impurities.

According to J. L. R. Morgan and W. A. Duff,[10] when two electrodes—one of chromium and one of platinum—are immersed in dil. sulphuric acid, the current passes freely when platinum is made the anode, but if chromium is made the anode no current passes through the cell. If the applied e.m.f. be gradually increased when chromium is the anode, no current passes until about 75 volts are attained; if the increase is made so rapid that the current passes from chromium to platinum, or if the cell is broken down by the application of more than 75 volts, it is an asymmetrical resistance when platinum is the anode, whilst if chromium is the anode the current passes freely; again, if too high an e.m.f. be applied to the platinum anode, another reversal occurs, and about 75 volts can again be stopped using chromium as anode. The chromium cell can also be used for the **rectification of alternating currents.** The phenomenon is attributed to the formation of a resistant film as in the case of the aluminium cell. W. Günther-Schulze studied the attraction of electrons for the CrO_4-ions. H. Nagaoka and T. Futagama studied the spluttering of chromium by the disruptive discharge in a magnetic field.

W. Ostwald found that when active chromium acts on acids, there is a **periodicity** in the rate of evolution of hydrogen. A piece of passive chromium rendered active by contact with cadmium under acid, was dissolved in 2N-HCl. The curve showing the rate of action is irregular for about 15 minutes, when it becomes periodic, the velocity rapidly increasing to a maximum and then falling more slowly to a minimum. The duration of each period increases during the progress of the reaction. Different forms of curve were obtained from different pieces of chromium; and two pieces placed in the same acid were found to give a double summation curve showing that the periodicity lies in the metal and not in the acid. An increase in the concentration of the acid causes an increase in the frequency of the periodic phenomena; the frequency is doubled by a rise of about 10°; the frequency is increased by the addition of oxidizing agents—*e.g.* nitric acid, nitrogen oxide, and chloric and bromic acids—and it is decreased by small amounts of formaldehyde or potassium cyanide. Dextrin and other carbohydrates help to bring about regular periodicity. No periodic phenomena were observed with the dissolution of iron, zinc, or manganese. The metal contained silicon, iron, sulphur, and carbon; but which of these is the active agent was not determined—purified chromium did not exhibit the phenomenon.

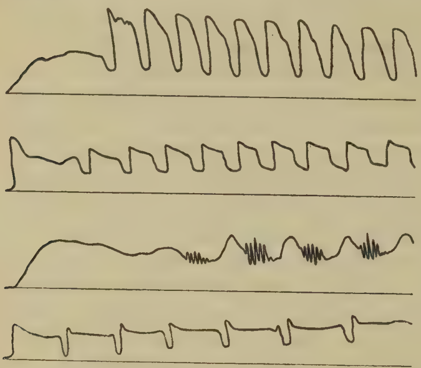


FIG. 5.—Periodic Evolution of Gas in the Dissolution of Chromium in Acids.

Nugatory attempts to render the metal active by the addition of cupric chloride, sodium sulphite, alcohol, ferrous chloride, ferric chloride, colloidal platinum, chromic acid, potassium nitrite; prolonged contact with metallic platinum; variation of temp. between 0° and 50°; previous treatment of the metal with chromic acid or potassium permanganate; fusion with potassium nitrate; heating on charcoal with sodium phosphate to give the metal a phosphorus content; melting in the electric oven in an atm. of coal-gas; using the metal as anode have all been made.

E. Brauer observed that the active chromium dissolving not only exhibits changes in its rate of evolution of hydrogen, but it also shows changes in its electric potential for the current produced by a cell of active chromium and platinum immersed in acid also varies periodically. The two sets of curves were analogous, but in some cases there is a variation in the electric properties when the evolution of hydrogen is apparently constant. The frequency increases with increasing conc. of acid, and is no longer apparent when the conc. of the acid is great enough. In one case, no periodicity was observed at 6°, periodicity was marked at 20°, and very pronounced at 31°. A piece of inactive chromium became active when rubbed with a piece of cadmium; and a slight activity was induced by the addition of arsenic or arsenic sulphides to the acid. E. Brauer attributes the periodicity to variations in the e.m.f. associated with the different oxidation stages of chromium. E. S. Hedges and J. E. Myers found that the addition of litharge would make chromium show the periodic phenomenon; they also showed that the periodic phenomenon is not due to the supersaturation of soln. or metal with gas; but is rather connected with the chemical change itself. The periodicity was shown to depend on the presence of a suitable catalytic agent and to be independent of the dissolving metal. The phenomenon was studied by B. Strauss and J. Hinnüber. W. Ogawa studied the action of chromium salts on galena as a radio-detector.

According to M. Faraday,[11] chromium is non-magnetic; this was not the conclusion of W. F. Barrett, but F. Wöhler, E. Glatzel, and H. Moissan found that the purified metal is non-magnetic. S. Curie studied the magnetization of iron with 2·5 to 3·4 per cent. of chromium; and K. Honda, of chromium with 20 per cent. of iron. M. Owen gave for the **magnetic susceptibility** of chromium $3{\cdot}16\times10^{-6}$ mass units; K. Ihde, 26×10^{-6} vol. unit; and K. Honda, $3{\cdot}7\times10^{-6}$ mass unit at 18°, and $4{\cdot}2\times10^{-6}$ mass units at 1100°. J. Weiss and H. K. Onnes found that at —25·9°, the magnetic properties of chromium are very feeble. E. Wiedemann found that the atomic magnetism of chromium in various salt soln. approximates 42 when that of iron in ferric chloride is 100. This result is independent of the nature of the anion associated with the chromium. W. Lepke found that with a field strength of *H* kgrms., the magnetic susceptibilities $\times 10^{-6}$ mass unit of massive and powdered chromium, are :

H .	1·0	3·3	7·0	10·0	16·0	18·0
Mass.	4·1	3·6	3·5	3·5	3·5	3·5
Powd.	4·3	5·4	4·2	4·1	4·0	3·9

P. Weiss and P. Collet calculated $63·3 \times 10^{-6}$ for the atomic permeability. J. Safranek found the magnetic susceptibility of chromium to be independent of the magnetic field between 2000 and 14,000 gauss and of the temp. between 100° and 600° and to have a value of $4·31 \times 10^{-6}$. The reciprocal of the susceptibility of the alloys plotted against temp. gives a straight line becoming concave towards the temp. axis at higher temp. The various magnetic constants are linear functions of the composition. P. S. Epstein found that the magnetic susceptibility of bivalent chromium is $7·9 \times 10^{-4}$ per unit mass ; and of tervalent chromium, $5·0 \times 10^{-4}$. Observations on the magnetic properties of chromium were also made by E. Wedekind, D. M. Bose, A. Dauvillier, R. H. Weber, and E. Feytis. P. Kapitza's observations on the effect of strong magnetic fields on the conductivity are summarized in Fig. 6. L. Rosenfeld discussed the relation between the magnetic susceptibility and the refractive index ; and E. C. Stoner, the magnetic moment. P. Weiss, and L. A. Welo studied the magnetism of chromium salts.

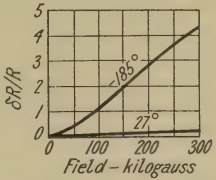


Fig. 6.—The Effect of Magnetic Fields on the Electrical Conductivity.

REFERENCES.

[1] A. J. Bradley and E. F. Ollard, *Nature*, **117**. 122, 1926 ; H. L. Cox and I. Backhurst, *Phil. Mag.*, (7), **7**. 981, 1929 ; W. Prinz, *Compt. Rend.*, **116**. 392, 1893 ; A. Binet du Jassonneix, *ib.*, **143**. 897, 1906 ; **144**. 915, 1907 ; E. Frémy, *ib.*, **44**. 433, 1857 ; H. Moissan, *ib.*, **116**. 349, 1893 ; **119**. 187, 1894 ; *Ann. Chim. Phys.*, (5), **21**. 199, 1880 ; *Bull. Soc. Chim.*, (2), **31**. 149, 1879 ; *Le four éléctrique*, Paris, 1897 ; London, 146, 1904 ; E. Glatzel, *Ber.*, **23**. 3127, 1890 ; E. Jäger and G. Krüss, *ib.*, **22**. 2052, 1889 ; E. Donath and J. Mayrhofer, *ib.*, **16**. 1588, 1883 ; P. A. Bolley, *Journ. Chem. Soc.*, **13**. 333, 1860 ; W. F. de Jong and H. W. V. Willems, *Physica*, **7**. 74, 1927 ; P. Vinassa, *Gazz. Chim. Ital.*, **58**. 178, 1928 ; E. Zettnow, *Pogg. Ann.*, **143**. 477, 1871 ; R. Bunsen, *ib.*, **91**. 619, 1854 ; *Ann. Chim. Phys.*, (3), **41**. 354, 1854 ; H. St. C. Deville, *ib.*, (3), **46**. 182, 1856 ; *Compt. Rend.*, **44**. 676, 1857 ; F. Wöhler, *Liebig's Ann.*, **111**. 230, 1859 ; E. C. Bain, *Trans. Amer. Inst. Min. Met. Eng.*, **68**. 625, 1922 ; J. E. Loughlin, *Amer. Journ. Science*, (2), **45**. 131, 1868 ; C. F. Rammelsberg, *Handbuch der krystallographisch-physikalischen Chemie*, Leipzig, **1**. 132, 1881 ; J. B. Richter, *Ueber die neueren Gegenstände der Chymie*, Breslau, **10**. 30, 1802 ; *Gehlen's Journ.*, **5**. 351, 1805 ; J. F. Gmelin, *Comment. Gött.*, **14**. 20, 1799 ; H. Moser, *Chemische Abhandlung über das Chrom*, Wien, 1824 ; *Schweigger's Journ.*, **42**. 99, 1842 ; T. Döring, *Journ. prakt. Chem.*, (2), **66**. 65, 1902 ; H. Schröder, *ib.*, (2), **19**. 266, 1879 ; K. W. Schwartz, *Trans. Amer. Electrochem. Soc.*, **44**. 451, 1923 ; E. M. Baker and A. M. Rente, *ib.*, **54**. 337, 1928 ; L. E. and L. F. Grant, *ib.*, **53**. 509, 1928 ; E. Schmid, *Zeit. Metallkunde*, **20**. 370, 1928 ; R. Blix, *Zeit. phys. Chem.*, **3**. B, 229, 1929 ; J. R. Rydberg, *Zeit. phys. Chem.*, **33**. 353, 1900 ; T. W. Richards, *ib.*, **61**. 183, 1908 ; *Journ. Amer. Chem. Soc.*, **37**. 470, 1643, 1915 ; T. W. Richards, F. N. Brink, and F. Bonnet, *ib.*, **31**. 154, 1909 ; F. Adcock, M. L. V. Gayler and P. N. Tucker, *Journ. Iron Steel Inst.*, **115**. i, 369, 1927 ; J. Disch, *Zeit. Physik*, **5**. 173, 1921 ; W. Widder, *Phys. Zeit.*, **26**. 618, 1925 ; F. Sillers, *Metal Ind.*, **30**. 533, 1927 ; **31**. 85, 1927 ; *Trans. Amer. Electrochem. Soc.*, **52**. 301, 1927 ; W. Treitschke and G. Tammann, *Zeit. anorg. Chem.*, **55**. 402, 1907 ; G. F. Hüttig and F. Brodkorb, *ib.*, **146**. 341, 1925 ; I. Traube, *ib.*, **8**. 12, 1895 ; K. Honda, *Ann. Physik*, (4), **32**. 1044, 1910 ; A. W. Hull, *Phys. Rev.*, (2), **14**. 540, 1919 ; (2), **17**. 571, 1921 ; R. A. Patterson, *ib.*, (2), **26**. 56, 1925 ; M. L. Huggins, *ib.*, (2), **21**. 509, 1925 ; (2), **28**. 1086, 1926 ; W. C. Phebus and F. C. Blake, *ib.*, (2), **25**. 107, 1925 ; W. P. Davey, *ib.*, (2), **21**. 716, 1923 ; W. P. Davey and T. A. Wilson, *ib.*, (2), **27**. 105, 1926 ; W. L. Bragg, *Phil. Mag.*, (6), **40**. 169, 1920 ; E. F. Ollard, *Metal Ind.*, **28**. 153, 511, 520, 1926 ; C. S. Smith, *ib.*, **28**. 456, 1926 ; H. G. Grimm, *Zeit. phys. Chem.*, **122**. 177, 1926 ; A. Gotta, *Ueber die Eigenschaften einiger Metallwasserstoff*, Leipzig, 1928 ; J. B. Dumas, *Traité de chimie appliquée aux arts*, Paris, **2**. 19, 1830 ; A. M. Berkenheim, *Zeit. phys. Chem.*, **141**. 35, 1929 ; V. M. Goldschmidt, *Skr. Norske Ud. Akad.*, 2, 1926 ; L. Pauling, *Journ. Amer. Chem. Soc.*, **49**. 765, 1927 ; E. T. Wherry, *Amer. Min.*, **14**. 54, 1929 ; R. J. Piersol, *Trans. Amer. Electrochem. Soc.*, **56**. 371, 1929 ; D. J. Smithells and S. V. Williams, *Nature*, **124**. 617, 1929 ; *Journ. Inst. Metals*, **40**. 273, 1929 ; F. Adcock, *Journ. Iron Steel Inst.*, **115**. i, 369, 1927 ; M. Grube, *Zeit. Ges. Giessereipr.*, **47**. 173, 1926 ; *Chim. Ind.*, **18**. 68, 1927 ;

P. W. Bridgman, *Proc. Amer. Acad.*, **62**. 218, 1928 ; F. C. Kelley, *Tech. Publ. Amer. Inst. Min. Eng.*, 89, 1928 ; J. Laissus, *Rev. Mét.*, **24**. 345, 1927 ; K. Ruf, *Zeit. Elektrochem.*, **34**. 813, 1928 ; D. J. Macnaughtan and A. W. Hothersall, *Journ. Electroplater's Tech. Soc.*, **5**. 63, 1930 ; D. J. Macnaughtan, *ib.*, **5**. 135, 1930 ; *Trans. Faraday Soc.*, **26**. 465, 1930 ; H. Shoji, *Kinzoku-no-Kenkyu*, **6**. 127, 1929 ; J. W. Slater, *Phys. Rev.*, (2), **36**. 57, 1930 ; W. Hume-Rothery, *Phil. Mag.*, (7), **10**. 217, 1930 ; W. van Drunen, *Ueber die Diffusion von Eisen mit Kobalt, Nickel und Chrom in festem Zustand*, Stuttgart, 1928.

[2] J. Disch, *Zeit. Physik*, **5**. 173, 1921 ; F. W. Adler, *Die Abhängkeit specifischen Wärme des Chroms von der Temperatur*, Zürich, 1902 ; W. Widder, *Phys. Zeit.*, **26**. 618, 1925 ; C. Forch and P. Nordmeyer, *Ann. Physik*, (4), **20**. 423, 1906 ; R. Lammel, *ib.*, (4), **16**. 551, 1905 ; P. Nordmeyer and A. L. Bernoulli, *Ber. deut. phys. Ges.*, **6**. 175, 1907 ; E. Jäger and G. Krüss, *Ber.*, **22**. 2052, 1889 ; F. Michand, *Compt. Rend.*, **171**. 241, 1920 ; H. Mache, *Sitzber. Akad. Wien*, **106**. 590, 1897 ; P. Chevenard, *Compt. Rend.*, **174**. 109, 1922 ; T. W. Richards and F. G. Jackson, *Zeit. phys. Chem.*, **70**. 414, 1910 ; H. Schimpff, *ib.*, **71**. 257, 1910 ; F. Simon and M. Ruhemann, *ib.*, **129**. 321, 1927 : S. Umino, *Science Rep. Tohoku Univ.*, **15**. 597, 1926 ; P. Schübel, *Zeit. anorg. Chem.*, **87**. 81, 1914 ; F. Wüst, A. Meuthen and R. Durrer, *Ver. deut. Ing. Forsch.*, 204, 1918 ; E. D. Eastman, A. M. Williams and T. F. Young, *Journ. Amer. Chem. Soc.*, **46**. 1184, 1924 ; J. Dewar, *Proc. Roy. Soc.*, **89**. A, 158, 1913 ; E. van Aubel, *Bull. Acad. Belg.*, (5), **7**. 155, 1921 ; G. F. Hüttig and F. Brodkorb, *Zeit. anorg. Chem.*, **146**. 341, 1925 ; J. Maydel, *ib.*, **178**. 113, 1929 ; **186**. 289, 1930 ; G. Tammann and A. Rohmann, *ib.*, **190**. 227, 1930.

[3] W. Treitschke and G. Tammann, *Zeit. anorg. Chem.*, **55**. 402, 1907 ; E. Tiede and E. Birnbräuer, *ib.*, **87**. 129, 1914 ; R. S. Williams, *ib.*, **53**. 1, 1907 ; G. Voss, *ib.*, **57**. 58, 1908 ; K. Lewkonja, *ib.*, **59**. 293, 1908 ; G. Hindrichs, *ib.*, **59**. 414, 1908 ; G. K. Burgess, *Bull. Bur. Standards*, **3**. 345, 1907 ; *Chem. News*, **97**. 28, 1908 ; G. K. Burgess and R. G. Waltenberg, *Journ. Washington Acad.*, **3**. 371, 1913 ; *Brass World*, **9**. 349, 1913 ; *Journ. Franklin Inst.*, **176**. 737, 1913 ; *Zeit. anorg. Chem.*, **82**. 361, 1913 ; R. Vogel and E. Trilling, *ib.*, **129**. 276, 1923 ; W. Herz, *ib.*, **170**. 237, 1928 ; A. von Vogesack, *ib.*, **154**. 30, 1926 ; S. O. Cowper-Cowles, *Chem. News*, **81**. 16, 1900 ; E. A. Lewis, *ib.*, **86**. 13, 1902 ; J. Johnston, *Journ. Ind. Eng. Chem.*, **9**. 873, 1917 ; H. Moissan, *Bull. Soc. Chim.*, (3), **35**. 947, 1906 ; *Le four électrique*, Paris, 1900 ; London, 146, 1904 ; *Compt. Rend.*, **142**. 428, 1906 ; H. St. C. Deville, *ib.*, **44**. 676, 1857 ; *Ann. Chim. Phys.*, (3), **46**. 182, 1856 ; C. J. Smithells and S. V. Williams, *Nature*, **124**. 617, 1929 ; *Journ. Inst. Metals*, **40**. 273, 1928 ; H. C. Greenwood, *Proc. Roy. Soc.*, **82**. A, 396, 1909 ; **83**. A, 1910 ; E. Newbery and J. N. Pring, *ib.*, **92**. A, 276, 1916 ; R. D. Kleeman, *Journ. Phys. Chem.*, **31**. 1669, 1927 ; F. Wüst, A. Meuthen and R. Durrer, *Ver. deut. Ing. Forsch.*, 204, 1918 ; *Zeit. Instrknde.*, **39**. 294, 1919 ; S. Umino, *Science Rep. Tohoku Univ.*, **15**. 597, 1926 ; E. Glatzel, *Ber.*, **23**. 3127, 1890 ; W. Guertler and M. Pirini, *Zeit. Metallkunde*, **11**. 1, 1919 ; L. I. Dana and P. D. Foote, *Trans. Faraday Soc.*, **15**. 186, 1920 ; G. N. Lewis, J. E. Gibson and W. M. Latimer, *Journ. Amer. Chem. Soc.*, **44**. 1008, 1922 ; E. D. Eastman, *ib.*, **45**. 80, 1923 ; E. D. Eastman, A. M. Williams and T. F. Young, *ib.*, **46**. 1184, 1924 ; B. Bruzs, *Journ. Phys. Chem.*, **31**. 681, 1927 ; W. R. Mott, *Trans. Amer. Electrochem. Soc.*, **34**. 255, 1918 ; K. Honda, *Ann. Physik*, (4), **32**. 1044, 1910 ; E. Kordes, *Zeit. anorg. Chem.*, **160**. 67, 1927 ; W. Herz, *ib.*, **177**. 116, 1928.

[4] A. L. Bernoulli, *Die Passivität des Chroms nach der Faradayschen Theorie*, München, 1904 ; *Phys. Zeit.*, **5**. 632, 1904 ; W. J. Pope, *Journ. Chem. Soc.*, **69**. 1530, 1896 ; J. H. Gladstone, *Proc. Roy. Soc.*, **16**. 439, 1868 ; **18**. 49, 1869 ; H. von Wartenberg, *Verh. deut. phys. Ges.*, **12**. 105, 1910 ; W. W. Coblentz, *Journ. Franklin Inst.*, **170**. 169, 1910 ; *Bull. Bur. Standards*, **7**. 198, 1911 ; W. W. Coblentz and R. Stair, *Journ. Research Bur. Standards*, **2**. 343, 1929 ; V. Fréedericksz, *Ann. Physik*, (4), **34**. 780, 1911 ; F. J. Michéli, *Arch. Science Genève*, (2), **10**. 117, 1900 ; M. Luckiesh, *Journ. Amer. Opt. Soc.*, **19**. 1, 1929 ; P. R. Gleason, *Proc. Nat. Acad.*, **15**. 551, 1929.

[5] T. Bayley, *Journ. Chem. Soc.*, **37**. 828, 1880 ; J. Piccard and E. Thomas, *Helvetica Chim. Acta*, **6**. 1040, 1923 ; W. Biltz, *Zeit. anorg. Chem.*, **127**. 169, 1923 ; M. C. Lea, *Chem. News*, **730**. 260, 271, 1896 ; *Zeit. anorg. Chem.*, **9**. 312, 1895 ; **12**. 249, 340, 1896 ; *Amer. Journ. Science*, (3), **49**. 357, 1895 ; I. Lifschitz and E. Rosenbohm, *Zeit. phys. Chem.*, **97**. 1, 1921 ; Y. Shibata, *Journ. Japan. Chem. Soc.*, **40**. 463, 1919 ; M. N. Saha, *Nature*, **125**. 163, 1930.

[6] K. Someya, *Zeit. anorg. Chem.*, **161**. 46, 1927 ; G. Kirchhoff, *Sitzber. Akad. Berlin*, 63, 1861 ; 227, 1863 ; H. Kayser, *Handbuch der Spectroscopie*, Leipzig, **5**. 337, 1910 ; **7**. i, 278, 1924 ; J. Formanek, *Die qualitative Spektralanalyse anorganischer und organischer Körper*, Berlin, 144, 1905 ; F. Gottschalk and E. Drechsel, *Journ. prakt. Chem.*, (1), **89**. 473, 1863 ; V. Merz, *ib.*, (1), **80**. 487, 1860 ; W. Miller, *Zeeman-Effect an Magnesium, Calcium, und Strontium*, Göttingen, 1906 ; *Ann. Physik*, (4), **24**. 105, 1907 ; A. Sommerfeld, *ib.*, (4), **70**. 32, 1923 ; W. A. Miller, *Phil. Mag.*, (3), **2**. 331, 1833 ; *Phil. Trans.*, **152**. 861, 1862 ; W. Huggins, *ib.*, **154**. 139, 1864 ; R. J. Lang, *Nature*, **118**. 119, 1926 ; *Phil. Trans.*, **224**. A, 371, 1924 ; W. de W. Abney and E. R. Festing, *ib.*, **172**. 887, 1881 ; D. Brewster, *ib.*, **125**. 91, 1835 ; *Phil. Mag.*, (4), **24**. 441, 1862 ; H. Croft, *ib.*, (3), **21**. 197, 1842 ; J. L. Soret, *Arch. Sciences Genève*, (2), **61**. 322, 1878 ; (2), **63**. 89, 1879 ; R. Thalén, *Om spectralanalys*, Upsala, 1866 ; *Nova Acta Upsala*, (3), **6**. 9, 1865 ; *Ann. Chim. Phys.*, (4), **18**. 202, 1869 ; H. Becquerel, *ib.*, (5), **30**. 5, 1883 ; J. Gay, *ib.*, (6), **5**. 145, 1885 ; H. Smith, *Phil. Mag.*, (6), **27**. 801, 1914 ; W. Ackroyd, *ib.*, (5), **2**. 423, 1876 ; H. E. Talbot, *ib.*, (3), **4**. 112, 1834 ; J. H. Gladstone, *ib.*, (4), **14**. 48, 1857 ; *Journ. Chem. Soc.*, **10**. 79, 1858 ; L. de Boisbaudran, *Spectres lumineux*, Paris, 1876 ; *Compt. Rend.*, **105**. 261, 1228, 1887 ; **106**. 178, 1888 ; **107**. 311, 468, 490, 1888 ;

A. Étard, *ib.*, **120**. 1057, 1895 ; G. J. Stoney and J. E. Reynolds, *Phil. Mag.*, (4), **42**. 41, 1871 ; G. D. Liveing and J. Dewar, *ib.*, (5), **18**. 161, 1884 ; *Proc. Roy. Soc.*, **32**. 402, 1881 ; **35**. 71, 1883 ; **36**. 471, 1884 ; J. N. Lockyer and W. C. Roberts-Austen, *ib.*, **23**. 344, 1875 ; J. N. Lockyer and F. E. Baxandall, *ib.*, **74**. 255, 1904 ; J. N. Lockyer, *ib.*, **43**. 117, 1887 ; **65**. 451, 1899 ; *Tables of Wave-lengths of Enhanced Lines*, London, 1906 ; *Phil. Trans.*, **172**. 561, 1881 ; W. N. Hartley, *ib.*, **185**. 161, 1898 ; *Proc. Roy. Soc.*, **21**. 499, 1873 ; *Trans. Roy. Soc. Dublin*, (2), **7**. 233 1900 ; *Chem. News*, **21**. 499, 1873 ; C. A. Schunck, *ib.*, **51**. 152, 1885 ; H. M. Vernon, *ib.*, **66**. 104, 114, 141, 152, 1892 ; C. de Watteville, *ib.*, **204**. 139, 1904 ; *Spectres de flammes—Variations spectrales d'ordre thermique*, Evreux, 1904 ; A. Gouy, *Compt. Rend.*, **85**. 439, 1877 ; P. Sabatier, *Journ. Phys.*, (2), **6**. 312, 1887 ; *Compt. Rend.*, **103**. 49, 138, 1886 ; H. Moissan, *ib.*, **93**. 1079, 1881 ; H. Deslandres, *ib.*, **188**. 669, 1929 ; A. Recoura, *ib.*, **102**. 515, 1886 ; **112**. 1439, 1891 ; A. de Gramont, *ib.*, **126**. 1513, 1898 ; **144**. 1101, 1907 ; **150**. 37, 1910 ; **155**. 276, 1912 ; **176**. 216, 1923 ; *Bull. Soc. Min.*, **20**. 376, 1899 ; J. Parry and A. E. Tucker, *Engg.*, **27**. 127, 429, 1879 ; **28**. 141, 1879 ; T. Bayley, *Journ. Chem. Soc.*, **37**. 828, 1880 ; T. Carnelley, *Ber.*, **17**. 2152, 1884 ; K. Vierordt, *Die Anwendung des Spectralapparates zur Photometrie*, Tälingen, 1873 ; *Ber.*, **5**. 34, 1872 ; H. W. Vogel, *ib.*, **21**. 2030, 1868 ; *Praktische Spektralanalyse irdischer Stoffe*, Berlin, 1883 ; C. Zimmermann, *Liebig's Ann.*, **213**. 285, 1882 ; E. L. Nichols, *Amer. Journ. Science*, (3), **28**. 342, 1884 ; A. Byk and H. Jaffe, *Zeit. phys. Chem.*, **68**. 323, 1909 ; W. Böhlendorff, *Studien zur Absorptions-spectralanalyse*, Erlangen, 1890 ; H. Bremer, *Einfluss der Temperatur gefärbter Lösungen auf die Absorptionsspectra derselben*, Erlangen, 1890 ; F. Hamburger, *Wied. Ann.*, **56**. 172, 1895 ; O. Knoblauch, *ib.*, **43**. 738, 1891 ; E. Wiedemann, *ib.*, **5**. 580, 1878 ; H. Settegast, *ib.*, **7**. 242, 1879 ; J. M. Hiebendaal, *Orderzoek over eenige absorptiespectra*, Utrecht, 1873 ; W. Lapraik, *Journ. prakt. Chem.*, (2), **47**. 305, 1893 ; F. Melde, *Pogg. Ann.*, **124**. 91, 1865 ; J. Müller, *ib.*, **72**. 76, 1847 ; **79**. 341, 1850 ; C. Pulfrich, *Zeit. Kryst.*, **6**. 142, 1882 ; G. Magnanini, *Gazz. Chim. Ital.*, **25**. ii, 373, 1895 ; G. Magnanini and T. Bentivoglio, *Atti Accad. Lincei*, (5), **2**. ii, 17, 1893 ; G. B. Rizzo, *Nuovo Cimento*, (3), **35**. 132, 1894 ; C. P. Smyth, *Trans. Roy. Soc. Edin.*, **28**. 779, 1879 ; T. Erhard, *Absorption des Lichtes in einigen Chromsalzen*, Freiberg, 1875 ; J. C. McLennan, *Trans. Roy. Soc. Canada*, (3), **19**. 89, 1925 ; G. Wentzel, *Phys. Zeit.*, **24**. 104, 1923 ; G. Joos, *ib.*, **29**. 117, 1928 ; V. Schumann, *Phot. Rend.*, **41**. 71, 1890 ; F. McClean, *Month. Notices Astron. Soc.*, **52**. 22, 1891 ; B. Hasselberg, *Svenska Akad. Handl.*, 24, 1894 ; H. Nagaoka and Y. Sugiura, *Japan. Journ. Phys.*, **3**. 45, 1924 ; *Science Papers Japan. Inst. Phys. Chem. Research.*, **2**. 139, 1924 ; M. Kimura and G. Nakamura, *ib.*, **3**. **51**. 1925 ; H. Nagaoka, D. Nukiyama and T. Futagami, *Proc. Acad. Japan*, **3**. 392, 398, 403, 409, 415, 1927 ; E. Demarçay, *Spectres électriques*, Paris, 1895 ; H. A. Rowland, *Preliminary Table of Solar Spectrum Wave-lengths*, Chicago, 1898 ; F. Exner and E. Haschek, *Wellenlängentabellen für spectralanalytische Untersuchungen auf Grund der ultravioletten Funkenspectra der Elemente*, Leipzig, 1904 ; *Wellenlängentabellen für spectralanalytische Untersuchungen auf Grund der ultravioletten Bogenspectren der Elemente*, Leipzig, 1904 ; *Die Spectren der Element bei normalen Druck*, Leipzig, 1912 ; A. E. Ruark and R. L. Chenault, *Phil. Mag.*, (6), **50**. 937, 1925 ; *Sitzber. Akad. Wien*, **106**. 1127, 1897 ; G. Ciamiacian, *ib.*, **76**. 499, 1877 ; J. M. Eder and E. Valenta, *ib.*, **118**. 1077, 1909 ; *Atlas typischer Spektren*, Wien, 1911 ; W. J. Humphreys, *Astrophys. Journ.*, **6**. 169, 1877 ; **26**. 18, 1907 ; R. E. Loving, *ib.*, **22**. 285, 1905 ; P. G. Nutting, *ib.*, **23**. 64, 1906 ; Lord Blythswood and W. A. Scoble, *ib.*, **24**. 125, 1906 ; F. L. Cooper, *ib.*, **29**. 329, 1909 ; H. D. Babcock, *Phys. Rev.*, (2), **22**. 200, 1923 ; *Astrophys. Journ.*, **33**. 217, 1911 ; **58**. 149, 1923 ; H. N. Russell, *ib.*, **66**. 184, 1927 ; D. Foster, *ib.*, **67**. 16, 1928 ; J. A. Anderson, *ib.*, **46**. 104, 1917 ; H. M. Randall and E. F. Barker, *ib.*, **49**. 54, 1919 ; A. S. King, *ib.*, **41**. 86, 1915 ; **45**. 254, 1917 ; **60**. 282, 1924 ; *Phys. Rev.*, (2), **5**. 79, 1915 ; (2), **29**. 359, 1927 ; *Proc. Nat. Acad.*, **2**. 461, 1916 ; N. Seljakoff and A. Krasnikoff, *Zeit. Physik*, **33**. 601, 1925 ; T. Dreisch, *ib.*, **40**. 714, 1927 ; H. E. White and R. C. Gibbs, *Proc. Nat. Acad.*, **12**. 675, 1926 ; *Phys. Rev.*, (2), **29**. 359, 426, 606, 654, 917, 1927 ; (2), **33**. 157, 1929 ; H. E. White, *ib.*, (2), **32**. 319, 1928 ; (2), **33**. 286, 538, 672, 915, 1098, 1929 ; R. V. Zumstein, *ib.*, (2), **27**. 562, 1926 ; R. A. Millikan and I. S. Bowen, *ib.*, (2), **23**. 1, 1924 ; E. O. Hulburt, *ib.*, (2), **24**. 129, 1924 ; (2), **25**. 888, 1925 ; A. W. Smith and M. Muskat, *ib.*, (2), **29**. 663, 1927 ; C. V. Raman and S. K. Datta, *Nature*, **115**. 946, 1925 ; A. B. McLay, *Trans. Roy. Soc. Canada*, (3), **17**. 137, 1923 ; W. Gerlach, *Festschrift des Phys. Ver.*, 45, 1924 ; E. Viterbi and G. Krausz, *Gazz. Chim. Ital.*, **57**. 690, 1927 ; W. E. Adeney, *Trans. Roy. Soc. Dublin*, (2), **7**. 331, 1901 ; *Proc. Roy. Soc. Dublin*, (2), **10**. 235, 1904 ; A. Hagenbach and H. Konen, *Atlas der Emissionsspectra*, Jena, 1905 ; O. Lohse, *Publ. Obs. Potsdam*, **12**. 109, 1902 ; B. Käbitz, *Ueber die Absorptionspectren der Chlorsauren*, Bonn, 1904 ; J. E. Purvis, *Proc. Cambridge Phil. Soc.*, **14**. 41, 1906 ; J. Clodius, *Die Wellenlängen des elementes Chrom im electrischen Flammenbogen*, Bonn, 1906 ; W. Hartmann, *Das Zeeman-Phänomen im sichtbaren Spectren von Kupfer, Eisen, Gold, and Chrom*, Halle, 1907 ; L. Stüting, *Untersuchungen über den rothen Theil der Bogenspectren von Nickel, Cobalt, und Chrom*, Bonn, 1909 ; *Zeit. wiss. Photochem.*, **7**. 73, 1909 ; H. Geiseer, *ib.*, **7**. 89, 1909 ; *Zur anomalen Dispersion des Lichtes in Metalldämpfen*, Bonn, 1909 ; H. Finger, *Ein Beitrag zur Kenntnis des Einflusses des Mediums auf die Linien in Funkenspectren*, Münster, 1909 ; *Zeit. wiss. Photochem.*, **7**. 330, 369, 1909 ; J. H. Pollock and A. G. G. Leonard, *Proc. Roy. Soc. Dublin*, (2), **11**. 217, 1907 ; J. H. Pollock, *ib.*, (2), **13**. 253, 1912 ; A. Duvallier, *Compt. Rend.*, **183**. 193, 1926 ; M. A. Catalan, *ib.*, **176**. 84, 1063, 1923 ; *Anal. Fis. Quim.*, **21**. 84, 213, 1923 ; **28**. 83, 611, 1930 ; L. Janicki, *Ann. Physik*, (4), **29**. 833, 1909 ; R. Frerichs, *ib.*, (4), **81**. 807, 1926 ; *Zeit. Physik*, **31**. 305, 1925 ; H. du Bois and G. J. Elias, *Ann. Physik*, (4), **35**. 617, 1911 ; O. Lüttig, *ib.*, (4), **38**. 43, 1912 ;

K. W. Meissner, *ib.*, (4), **50**. 713, 1916 ; M. Steenbeck, *ib.*, (4), **87**. 811, 1928 ; H. Ceiseler, *ib.*, (4), **69**. 147, 1922 ; *Zeit. Physik*, **22**. 228, 1924 ; H. Gieseler and W. Grotrian, *ib.*, **22**. 245, 1924 ; E. Krömer, *ib.*, **52**. 531, 1928 ; W. C. van Geel, *ib.*, **33**. 836, 1925 ; O. Laporte, *ib.*, **39**. 123, 1926 ; R. Mecke, *ib.*, **42**. 390, 1927 ; A. Hantzsch and R. H. Clark, *Zeit. phys. Chem.*, **63**. 367, 1908 ; A. Hantzsch, *ib.*, **72**. 362, 1910 ; H. Fromherz, *ib.*, **1**. B, 301, 1928 ; A. Dufour, *Le Radium*, **6**. 298, 1909 ; **7**. 74, 1910 ; *Journ. Phys.*, (4), **9**. 277, 1919 ; *Compt. Rend.*, **150**. 614, 1910 ; *ib.*, **148**. 1594, 1909 ; F. Croze, *ib.*, **177**. 1285, 1923 ; L. and E. Bloch, *Journ. Phys. Rad.*, (6), **6**. 154, 1925 ; F. E. Baxandall, *Researches on the Chemical Origin of Various Lines in Solar and Stellar Spectra*, London, 1910 ; H. C. Jones and W. W. Strong, *Amer. Chem. Journ.*, **43**. 37, 1910 ; C. Wali-Mohammad, *Untersuchungen über Struktur und magnetische Zerlegung seiner Spectrallinien im Vakuumlichtbogen*, Göttingen, 1912 ; N. Seljakoff and A. Krasnikoff, *Nature*, **117**. 554, 1926 ; K. Burns, *Bull. Lick. Obs.*, 27, 1913 ; *Zeit. wiss. Photochem.*, **12**. 207, 1913 ; **13**. 235, 1913 ; *Publ. Allegheny Obs.*, **8**. 1, 1930 ; R. Richter, *Zeemaneffekt an Chrom vom ultravioletten bis zum blauen Teil des Spektrums, unter besonderer Berücksichtigung einiger Asymmetrien*, Göttingen, 1914 ; S. P. de Rubies, *Anal. Fis. Quim.*, **15**. 110, 1917 ; J. Buchholz, *Das Bogenspektrum von Titan gemessen nach internationalen Normalen*, Bonn, 1913 ; H. Bracchetti, *Ueber die kathodische Herstellung von Metallspiegeln*, Münster, 1920 ; H. Pickhan, *Tertiären Normalen*, Münster, 1920 ; J. Hall, *Das Bogenspectrum des Chrom*, Bonn, 1921 ; C. C. Kiess and W. F. Meggers, *Bull. Bur. Standards*, **16**. 51, 1920 ; *Scient. Paper Bur Standards*, 272, 1920 ; C. C. and H. Kiess, *Science*, (2), **56**. 666, 1922 ; C. C. Kiess and O. Laporte, *ib.*, (2), **63**. 234, 1926 ; C. C. Kiess, *Journ. Research Bur. Standards*, **1**. 75, 1928 ; **5**. 775, 1930 ; W. F. Meggers, C. C. Kiess and F. M. Walters, *Journ. Amer. Opt. Soc.*, **9**. 355, 1924 ; Y. M. Woo, *Phys. Rev.*, (2), **22**. 428, 1926 ; S. Goudsmit, *ib.*, (2), **31**. 946, 1928 ; T. Tanaka, *Journ. Amer. Opt. Soc.*, **8**. 501, 1924 ; A. Mitscherlich, *Pogg. Ann.*, **121**. 459, 1864 ; S. Kato, *Science Papers Japan. Inst. Phys. Chem. Research*, **13**. 7, 1930 ; M. Edlen and M. Ericson, *Compt. Rend.*, **190**. 173, 1930 ; C. E. Hesthal, *Phys. Rev.*, (2), **35**. 126, 1930.

[7] M. Levi, *Trans. Roy. Soc. Canada*, (3), **18**. 159, 1924 ; B. Kievit and G. A. Lindsay, *Phys. Rev.*, (2), **35**. 292, 1930 ; (2), **36**. 648, 1930 ; J. H. van Vleck and A. Frank, *ib.*, (2), **34**. 1495, 1929 ; H. R. Robinson and C. L. Young, *Phil. Mag.*, (7), **10**. 71, 1930 ; R. C. Gibbs and H. E. White, *Proc. Nat. Acad.*, **13**. 525, 1927 ; *Phys. Rev.*, (2), **29**. 917, 1927 ; M. Siegbahn and W. Stenström, *Phys. Zeit.*, **17**. 48, 318, 1916 ; M. Siegbahn, *Phil. Mag.*, (6), **37**. 601, 1919 ; *Ann. Physik*, (4), **59**. 56, 1919 ; *Jahrb. Rad. Elektron.*, **13**. 296, 1916 ; **18**. 240, 1922 ; E. Rupp, *Ann. Physik*, (5), **1**. 773, 1929 ; M. Steenbeck, *ib.*, (4), **87**. 811, 1928 ; C. E. Howe, *Phys. Rev.*, (2), **33**. 1088, 1929 ; (2), **35**. 717, 1930 ; B. C. Mukherjee and B. B. Ray, *Zeit. Physik*, **57**. 545, 1929 ; G. Kellström, *ib.*, **58**. 511, 1929 ; V. Dolejsck, *Compt. Rend.*, **174**. 441, 1922 ; V. Dolejsek and K. Pestrecoff, *Zeit. Physik*, **53**. 566, 1929 ; M. Siegbahn and V. Dolejsek, *ib.*, **10**. 159, 1922 ; D. Coster, *ib.*, **25**. 83, 1924 ; A. E. Lindh, *ib.*, **31**. 210, 1925 ; N. Stensson, *ib.*, **3**. 60, 1920 ; S. Eriksson, *ib.*, **48**. 360, 1928 ; F. Hjalmar, *ib.*, **1**. 439, 1921 ; *Phil. Mag.*, (6), **41**. 675, 1921 ; R. Thoroeus, *ib.*, (7), **1**. 312, 1926 ; (7), **2**. 1007, 1926 ; R. Thoroeus and M. Siegbahn, *Arkiv. Nat. Astron. Fys.*, **19**. A, 12, 1925 ; W. Duane and Kang-Fuh-Hu, *Phys. Rev.*, (2), **14**. 516, 1919 ; H. Fricke, *ib.*, (2), **16**. 202, 1920 ; W. Duane and H. Fricke, *ib.*, (2), **17**. 529, 1921 ; E. C. Unnewehr, *ib.*, (2), **22**. 529, 1923 ; K. Chamberlain, *ib.*, (2), **26**. 525, 1925 ; Y. M. Woo, *ib.*, (2), **28**. 426, 1926 ; F. L. Hunt, *ib.*, (2), **29**. 919, 1927 ; (2), **30**. 227, 1927 ; T. L. de Bruin, *Arch. Néerl.*, (3), **11**. 70, 1928 ; F. P. Mulder, *ib.*, (3), **11**. 167, 1928 ; F. Wisshak, *Ann. Physik*, (5), **6**. 507, 1930 ; W. Bothe, *Phys. Zeit.*, **29**. 891, 1928 ; J. Schrör, *Ann. Physik*, (4), **80**. 297, 1926 ; G. Wentzel, *Naturwiss.*, **10**. 369, 464, 1922 ; B. Rosen, *ib.*, **14**. 978, 1926 ; O. Stelling, *Zeit. phys. Chem.*, **117**. 185, 1925 ; *Ber.*, **60**. B, 650, 1927 ; C. G. J. Moseley, *Phil. Mag.*, (4), **27**. 1024, 1913 ; N. Seljakoff and A. Krasnikoff, *Zeit. Physik*, **33**. 601, 1925 ; N. Seljakoff, A. Krasnikoff and T. Stellezky, *ib.*, **45**. 548, 1927 ; G. Kettmann, *ib.*, **18**. 359, 1923 ; **53**. 198, 1929 ; B. Walter, *ib.*, **30**. 357, 1924 ; M. J. Druyvesteyn, *ib.*, **43**. 707, 1927 ; H. Beuthe, *ib.*, **60**. 603, 1930 ; F. de Boer, *Arch. Néerl.*, (3), **5**. 101, 1927 ; H. N. Russell, *Astrophys. Journ.*, **66**. 233, 1927 ; A. Duvallier, *Compt. Rend.*, **183**. 193, 1926 ; S. Pastorello, *Nuovo Cimento*, (7), **6**. 50, 1929.

[8] R. Whiddington, *Proc. Cambridge Phil. Soc.*, **16**. 150, 1911 ; *Proc. Roy. Soc.*, **85**. A, 323, 1911 ; O. W. Richardson and F. S. Robertson, *ib.*, **115**. A, 280, 1927 ; **124**. A, 188, 1929 ; U. Nakaya, *ib.*, **124**. A, 616, 1929 ; C. A. Sadler and A. J. Steven, *Phil. Mag.*, (6), **21**. 659, 1911 ; C. G. Barkla and C. A. Sadler, *Phil. Mag.*, (6), **17**. 739, 1909 ; J. E. P. Wagstaff, *ib.*, (6), **47**. 84, 1924 ; T. E. Aurén, *ib.*, (6), **33**. 471, 1917 ; M. A. Catalan, *Compt. Rend.*, **176**. 1063, 1923 ; P. Weiss and G. Foex, *ib.*, **187**. 744, 1928 ; A. Poirot, *ib.*, **189**. 150, 1929 ; U. Andrewes, A. C. Davies and F. Horton, *Proc. Roy. Soc.*, **110**. A, 64, 1920 ; **117**. A, 649, 1928 ; *Phil. Mag.*, (7), **2**. 1253, 1926 ; E. C. Unnewehr, *Phys. Rev.*, (2), **22**. 529, 1923 ; D. M. Bose, *ib.*, (2), **27**. 521, 1926 ; A. Wehnelt, *Ann. Physik*, (4), **14**. 425, 1904 ; E. Rupp, *ib.*, (4), **85**. 981, 1928 ; B. B. Ray and R. C. Mazumdar, *Nature*, **123**. 49, 1929 ; *Zeit. Physik*, **53**. 646, 1929 ; R. H. Ghosh, *Journ. Indian Chem. Soc.*, **4**. 423, 1927 ; J. C. McLennan, *Proc. Nat. Acad.*, **12**. 726, 1926 ; W. Herz, *Zeit. anorg. Chem.*, **170**. 237, 1928 ; **177**. 116, 1928 ; H. N. Russell, *Astrophys. Journ.*, **66**. 233, 1927 ; E. Rabinowitsch and E. Thilo, *Zeit. phys. Chem.*, **6**. B, 284, 1929 ; W. Espe, *Ann. Physik*, (5), **2**. 381, 1929 ; R. E. Nyswander and B. E. Cohn, *Journ. Amer. Optical Soc.*, **20**. 131, 1930.

[9] J. J. Berzelius, *Liebig's Ann.*, **49**. 247, 1844 ; *Handl. Akad. Stockholm*, 1, 1843 ; *Pogg. Ann.*, **61**. 1, 1844 ; *Taylor's Scient. Memoirs*, **4**. 240, 1846 ; R. Bunsen, *Pogg. Ann.*, **91**. 619,

1854; *Ann. Chim. Phys.*, (3), **41**. 354, 1854; W. Muthmann and F. Fraunberger, *Sitzber. Akad. München*, (2), **34**. 201, 212, 1904; W. Hittorf, *ib.*, (1), **71**. 193, 1898; *Zeit. Elektrochem.*, **6**. 61, 1899; *Zeit. phys. Chem.*, **25**. 729, 1898; **30**. 481, 1899; **34**. 385, 1900; W. Rathert, *ib.*, **86**. 567, 1914; F. Flade, *Ueber die Passivität bei Eisen, Nickel und Chrom*, Marburg, 1910; *Zeit. phys. Chem.*, **88**. 569, 1914; R. Luther, *ib.*, **36**. 386, 1901; E. Grave, *Neue Untersuchungen über die Passivität von Metallen*, Leipzig, 1911; *Zeit. phys. Chem.*, **77**. 513, 1911; A. Adler, *ib.*, **80**. 385, 1912; W. J. Müller and E. Noack, *Monatsh.*, **48**. 293, 1927; W. J. Müller and O. Löwy, *ib.*, **48**. 711, 1927; **49**. 46, 1928; **50**. 385, 1928; **61**. 73, 1929; W. J. Müller and K. Knopicky, *ib.*, **48**. 711, 1927; **52**. 289, 1929; W. J. Müller, *Zeit. phys. Chem.*, **48**. 577, 1904; *Ber. deut. phys. Ges.*, **4**. 545, 1907; *Zeit. Elektrochem.*, **10**. 518, 1904; **30**. 401, 1924; **33**. 401, 1927; **34**. 850, 1928; **35**. 93, 1929; G. Grube, R. Heidinger and L. Schlecht, *ib.*, **32**. 70, 1926; G. Grube and L. Schlecht, *ib.*, **32**. 178, 1926; G. Grube, *ib.*, **33**. 389, 1927; G. Grube and G. Breitinger, *ib.*, **33**. 112, 1927; B. Strauss and J. Hinnüber, *ib.*, **34**. 407, 1928; J. Hinnüber, *ib.*, **34**. 852, 1928; **35**. 95, 1929; H. Eggert, *ib.*, **33**. 94, 1927; E. Müller, *ib.*, **33**. 72, 1927; E. Liebreich, *Brit. Pat. No.* 243246, 1924; 237288, 1925; *Korrosion Metallschutz*, **2**. 38, 1926; *Zeit. Electrochem.*, **33**. 69, 1927; **34**. 41, 1928; E. Liebreich, *ib.*, **27**. 94, 1921; T. Murakami, *Journ. Japan. Chem. Soc.*, **31**. 132, 1928; P. Kapitza, *Proc. Roy. Soc.*, **123**. A, 292, 342, 1929; F. J. Micheli, *Arch. Sciences Genève*, (4), **10**. 122, 1900; B. Neumann and G. Glaser, *Zeit. Elektrochem.*, **7**. 656, 1901; C. Fredenhagen, *Zeit. phys. Chem.*, **63**. 1, 1908; *Zeit. Elektrochem.*, **11**. 859, 1905; O. Sackur, *ib.*, **10**. 841, 1904; **12**. 637, 1906; J. Alvarez, *ib.*, **15**. 143, 1909; B. Neumann, *ib.*, **7**. 656, 1901; H. Kuessner, *ib.*, **16**. 754, 1910; *Ueber das anodische Verhalten des Molybdäns, Mangans, Chroms und Tantals*, Halle a. S., 1910; A. Burger, *Ber.*, **39**. 4071, 1906; K. F. Herzfeld, *Phys. Rev.*, (2), **29**. 701, 1927; F. Krüger and E. Nähring, *Ann. Physik*, (4), **84**. 939, 1927; E. Nähring, *Röntgenographische Untersuchungen über die Wasserstoffabsorption von Palladium und Palladium-Silber-Legierungen, und uber die Passivität von Eisen, Nickel, und Chrom*, Greisswald, 1928; L. McCulloch, *Trans. Amer. Electrochem. Soc.*, **56**. 325, 1929; W. Ogawa, *Journ. Japan. Soc. Chem., Ind.* **31**. 486, 1928; T. Döring, *Journ. prakt. Chem.*, (2), **66**. 69, 1902; (2), **73**. 393, 1906; G. C. Schmidt, *Chem. News*, **109**. 38, 1914; *Zeit. phys. Chem.*, **106**. 105, 1923; A. L. Bernoulli, *Die Passivität des Chroms nach der Faradayschen Theorie*, München, 1904; *Phys. Zeit.*, **5**. 632, 1904; C. W. Bennett and W. S. Burnham, *Trans. Amer. Electrochem. Soc.*, **29**. 217, 1916; S. J. French and L. Kahlenberg, *ib.*, **54**. 163, 1928; *Metal Ind.*, **33**. 443, 543, 569, 1928; A. Heydweiller, *Zeit. phys. Chem.*, **89**. 281, 1915; A. Theil and W. Hammerschmidt, *Zeit. anorg. Chem.*, **132**. 15, 1923; A. H. W. Aten, *Proc. Acad. Amsterdam*, **20**. 812, 1119, 1918; **21**. 138, 1918; P. E. Shaw and C. S. Jex, *Proc. Roy. Soc.*, **118**. A, 97, 1928; U. Sborgi and G. Cappon, *Nuovo Cimento*, (6), **23**. 303, 1922; Z. A. Epstein, *Zeit. Physik*, **32**. 620, 1925; N. Isgarischeff and A. Obrutscheva, *Zeit. Elektrochem.*, **29**. 428, 1923; A. M. Hasebrink, *ib.*, **34**. 819, 1928; E. Liebreich and W. Wiederholt, *ib.*, **30**. 263, 1924; **32**. 261, 263, 1926; E. Becker and H. Hilberg, *ib.*, **31**. 31, 1925; N. Bouman, *Rec. Trav. Chim. Pays-Bas.*, **43**. 1, 399, 1924; J. C. McLennan and C. D. Niven, *Phil. Mag.*, (7), **4**. 386, 1927; J. C. McLennan, C. D. Niven and J. O. Wilhelm, *ib.*, (7), **6**. 672, 1928; J. C. McLennan, *Proc. Nat. Acad.*, **12**. 726, 1926; A. Schulze, *Zeit. Metallkunde*, **15**. 155, 1923; G. Tammann and J. Hinnüber, *Zeit. anorg. Chem.*, **160**. 257, 1927; A. Günther-Schulze, *Zeit. Physik*, **3**. 349, 1920; A. Meyer, *Ueber Passivität der Metalle*, Osnabrück, 1919; K. Hopfgartner, *Monatsh.*, **40**. 259, 1919; E. Newbery, *Journ. Chem. Soc.*, **125**. 511, 1924; *Proc. Roy. Soc.*, **114**. A, 103, 1927; A. S. Russell, *Nature*, **115**. 455, 1924; **117**. 47, 1925; U. R. Evans, *ib.*, **121**. 351, 1928; *Journ. Soc. Chem. Ind.*, **49**. T, 68, 93, 1930; L. C. Bannister and U. R. Evans, *Journ. Chem. Soc.*, 1361, 1930; M. Centnerszwer and M. Straumanis, *Zeit. phys. Chem.*, **118**. 438, 1925; I. I. Shukoff, *Journ. Russ. Phys. Chem. Soc.*, **42**. 40, 1910; W. Koboseff and N. L. Nebrassoff, *Zeit. Elektrochem.*, **36**. 529, 1930; U. Sborgi and A. Borgia, *Gazz. Chim. Ital.*, **60**. 449, 1930; P. W. Bridgman, *Proc. Amer. Acad.*, **64**. 51, 1929.

[10] J. L. R. Morgan and W. A. Duff, *Journ. Amer. Chem. Soc.*, **22**. 331, 1900; E. Newbery, *Proc. Roy. Soc.*, **114**. A, 103, 1917; H. Nagaoka and T. Futagama, *Proc. Acad. Tokyo*, **3**. 643, 1927; W. Ostwald, *Zeit. phys. Chem.*, **35**. 33, 204, 1900; E. Brauer, *ib.*, **38**. 441, 1901; E. S. Hedges and J. E. Myers, *Journ. Chem. Soc.*, **125**. 604, 1924; *The Problem of Physico-Chemical Periodicity*, London, 1926; A. Günther-Schulze, *Zeit. Physik*, **3**. 349, 1920; B. Strauss and J. Hinnüber, *Zeit. Elektrochem.*, **34**. 407, 1928; W. Ogawa, *Journ. Japan. Soc. Chem. Ind.*, **31**. 486, 1928.

[11] S. Curie, *Bull. Soc. Enc. Nat. Ind.*, (5), **2**. 36, 1897; *Compt. Rend.*, **125**. 1165, 1897; J. Weiss and H. K. Onnes, *ib.*, **130**. 687, 1910; E. Feytis, *ib.*, **156**. 886, 1913; P. Collet, *ib.*, **181**. 1057, 1925; P. Weiss and P. Collet, *ib.*, **178**. 2146, 1924; A. Dauvillier, *ib.*, **176**. 1802, 1923; J. Safranek, *ib.*, **178**. 474, 1924; P. Pascal, *ib.*, **147**. 242, 742, 1908; W. F. Barrett, *Phil. Mag.*, (4), **46**. 478, 1873; E. C. Stoner, *ib.*, (7), **8**. 250, 1929; M. Faraday, *Phil. Trans.*, **136**. 41, 1846; *Phil. Mag.*, (3), **8**. 177, 1836; F. Wöhler, *Liebig's Ann.*, **111**. 230, 1859; E. Glatzel, *Ber.*, **23**. 3127, 1890; H. Moissan, *Bull. Soc. Chim.*, (3), **35**. 947, 1906; *Le four électrique*, Paris, 1900; London, 146, 1904; *Compt. Rend.*, **142**. 428, 1906; K. Honda, *Science Rep. Tohoku Univ.*, **1**. 1, 1912; **2**. 25, 1913; **3**. 139, 223, 1914; **4**. 215, 1915; *Ann. Physik*, (4), **32**. 1027, 1910; M. Owen, *ib.*, (4), **37**. 657, 1912; R. H. Weber, *ib.*, (4), **36**. 624, 1912; K. Ihde, *Untersuchugen über die Magnetisierbarkeit von Mangan, Mangankupfer und Chrom*, Marburg, 1912; L. Rosenfeld, *Naturwiss.*, **17**. 49, 1929; P. Kapitza, *Proc. Roy. Soc.*, **123**. A, 292, 342, 1929; W. Lepke, *Untersuchungen über die Magnetisierbarkeit von Mangan und Chrom in massivem und pulverförmigem Zustande*, Marburg,

1913; G. Jäger and S. Meyer, *Wied. Ann.*, **67**. 427, 707, 1899; E. Wiedemann, *ib.*, **32**. 452, 1887; P. S. Epstein, *Phys. Rev.*, (2), **22**. 204, 1923; L. A. Welo, *ib.*, (2), **32**. 320, 1928; D. M. Bose, *Zeit. Physik*, **43**. 864, 1927; E. Wedekind, *Zeit. angew. Chem.*, **37**. 87, 1924; P. Weiss, *Trans. Amer. Electrochem. Soc.*, **55**. 75, 1929.

§ 5. The Chemical Properties of Chromium

H. Moissan[1] studied the chemical affinity of chromium and the iron family of elements. F. Fischer and F. Schrötter observed no reaction when chromium is sparked beneath liquid **argon.** H. R. Carveth and B. E. Curry found that electro-deposited chromium can occlude about 250 times its vol. of hydrogen; in one experiment 24·6 c.c. of the gas were obtained from 0·698 c.c. of metal. E. Martin measured the occlusion of hydrogen by chromium. According to G. F. Hüttig and F. W. Brodkorb, electrolytic chromium deposited at —50° may contain 0·45 per cent. of hydrogen, in supersaturated solid soln. At the ordinary temp., the hydrogen press. of this chromium is less than 1·0 mm., but at 58° a sudden evolution of hydrogen takes place, although a temp. of 350° is required in order to remove the whole of the gas. No reproducible relations between temp., press., and hydrogen conc. could be established. T. Weichselfelder and B. Thiede obtained **chromium trihydride,** CrH_3, as a black precipitate, by the action of hydrogen on an ethereal soln. of phenylmagnesium bromide, C_6H_5MgBr, in which the dry metal chloride is suspended. The sp. gr. is 6·77. W. Biltz discussed the mol. vol. According to H. Gruber, a sheet of electrolytically-deposited chromium will slowly evolve occluded hydrogen if placed in boiling water, and if held in a Bunsen flame it will appear to take fire and burn on the surface with a pale blue non-luminous flame, although the metal remains sufficiently cool to avoid being oxidized. A. Sieverts and A. Gotta studied this subject. The heat of formation of chromium hydride is 3800 cals. per mol. of hydrogen; and the sp. gr. is 6·7663 to 6·7708.

A. L. Bernoulli said that chromium absorbs oxygen from **air** and so acquires the surface film of oxide. The behaviour of chromium in air depends on its state of subdivision; there is pyrophoric chromium; the specimen obtained by L. N. Vauquelin slowly oxidized when heated in air; that obtained by A. Binet du Jassonneix glowed like tinder in **oxygen** at 300°; that obtained by F. Wöhler when heated in air became yellow, then blue, and finally acquired a crust of green chromic oxide; and that obtained by H. Moissan was unaltered by exposure to dry air, but in moist air the well-polished surface acquired a slight tarnish, owing to the formation of a superficial film which does not penetrate deeper into the metal. This subject was discussed by N. B. Pilling and R. E. Bedworth. H. P. Walmsley examined the nature of the sesquioxide obtained as smoke from the chromium arc. Unlike molybdenum, chromium was found by C. Matignon and G. Desplantes not to be oxidized when the finely-divided metal is shaken up with aq. ammonia in air. When heated by the tip of the oxyhydrogen blowpipe flame, chromium burns yielding brilliant sparks; and when heated to 2000° in oxygen, it burns with the production of numerous sparks, more brilliant than those of iron. N. B. Pilling and R. E. Bedworth studied the rate of oxidation of chromium. F. Wöhler observed that chromium gives sparks and burns to chromic oxide when heated by the flame of a spirit-lamp fed with oxygen. H. W. Underwood described the use of chromium as an oxidation catalyst. H. V. Regnault, and F. Wöhler found that it decomposes when heated to bright redness in the vapour of **water,** forming hydrogen, and chromic oxide; and J. J. Berzelius found that the metal is not oxidized by boiling water. The action of **hydrogen dioxide** was found by L. J. Thénard to be at first feeble but later more vigorous. Part of the oxygen is given off free, and part combines with the metal. W. Guertler and T. Liepus observed no reaction by 48 hrs.' exposure to sea-water, aerated sea-water, or aerated rain-water. W. G. Mixter observed that no perchromate is formed by the action of **sodium dioxide** on chromium.

According to F. Wöhler, chromium glows when heated in **chlorine,** forming violet chromic chloride; and H. Moissan said that the reaction occurs at 600°. The red-hot metal is also attacked by **bromine** vapour—*vide infra,* chromic bromide; and with **iodine** vapour. W. Hittorf observed that chlorine and bromine make chromium passive, while R. Hanslian found that the presence of chromium does not affect the f.p. or b.p. of iodine. G. Tammann studied the action of iodine vapour on chromium. W. Guertler and T. Liepus observed no reaction with 48 hrs.' exposure to sat. chlorine-water. C. Poulenc found that **hydrogen fluoride** converts the red-hot metal into chromous fluoride; and C. E. Ufer observed that with **hydrogen chloride,** chromous chloride is formed. J. J. Berzelius found that the metal dissolves in **hydrofluoric acid,** particularly when warm, and hydrogen is given off. F. Wöhler, E. Jäger and G. Krüss, J. J. Berzelius, H. St. C. Deville, etc., noted that the metal dissolves in **hydrochloric acid** with the evolution of hydrogen and the formation of chromous chloride. W. Guertler and T. Liepus observed no reaction in less than 8 hrs. with 10 and 36 per cent. hydrochloric acid—*vide supra,* the passive state. H. Moissan said that hydrochloric acid attacks the metal slowly in the cold, and rapidly when heated, while the dil. acid has no action at ordinary temp., but on boiling, the attack is vigorous. W. Rohn found that 10 per cent. hydrochloric acid dissolves 77·4 grms. per sq. dm. per hr. during 24 hrs. in the cold and 150 grms. per sq. dm. per hr. when hot; and D. F. McFarland and O. E. Harder, that the normal acid dissolves 16,976·4 mgrms. per week per sq. in. W. Hittorf observed that chromium dissolves in hydrofluoric and hydrochloric acids as well as in **hydrobromic acid and hydriodic acid,** forming chromous salts and hydrogen. T. Döring said that the less pure the chromium prepared by the alumino-thermite process, the more quickly is it dissolved by the halide acid. The chromous chloride formed by the soln. of chromium in hydrochloric acid is converted, by a secondary reaction, into chromic chloride, the change being complete if the reaction is carried out at the ordinary temp., but less than complete if at 100°. This change is ascribed to a catalytic action of silica. If air is excluded, chromous chloride is stable in neutral soln., but in hydrochloric acid soln. it has a tendency to form chromic chloride; the reaction, which is accompanied by evolution of hydrogen, is extremely slow, but is markedly accelerated by addition of platinum black, finely-divided gold, or silica. The formation of chromic chloride from chromous chloride in acid soln. takes place according to the equation: $2CrCl_2+2HCl\rightleftharpoons2CrCl_3+H_2$, and is a reversible reaction. W. Hittorf found that chromium becomes passive in **chloric acid,** and in **perchloric acid.**

H. Moissan observed that chromium filings become incandescent if heated to 700° in **sulphur** vapour, and chromium sulphide is formed; and when heated to 1200° in a current of **hydrogen sulphide,** crystals of chromium sulphide are formed. W. Guertler and T. Liepus observed no reaction with 48 hrs.' exposure to 10 and 50 per cent. soln. of **sodium sulphide** with or without the addition of alkali-lye. N. Domanicky found that chromium is not readily attacked by an ethereal soln. of **sulphur monochloride;** and E. H. Harvey, that it is not attacked in a year at room temp. J. Férée said that pyrophoric chromium unites with **sulphur dioxide** with incandescence. H. V. Regnault, E. M. Péligot, H. Moissan, W. Hittorf, F. Wöhler, and E. Jäger and G. Krüss noted that chromium is but slowly attacked by dil. **sulphuric acid** in the cold, the action is slow even when hot, hydrogen is given off, and, if the action takes place out of contact with air, blue crystals of chromous sulphate can be obtained from the soln. Boiling, conc. sulphuric acid with chromium gives off sulphur dioxide. W. Guertler and T. Liepus observed no action in 48 hrs. with 10 per cent. H_2SO_4 and with 20 per cent. H_2SO_4 sat. with sodium sulphate. W. Rohn found that 10 per cent. sulphuric acid dissolves 0·01 grm. per sq. dm. per 24 hrs. in the cold, and 45 grms. per sq. dm. per hr. when hot; and D. F. McFarland and O. E. Harder, that the normal acid dissolves 1·00 mgrm. per sq. in. per week. J. Voisin, and A. Burger studied the action of sulphuric acid on the metal. G. Walpert observed that the rate of dissolution and the electrode potential of chromium in $4N$-H_2SO_4—unlike the case with iron (*q.v.*)—is raised by the addition of small proportions of potassium or sodium chloride, bromide, and iodide, and the period of induction is shortened. The addition of larger proportions of these salts may act in the reverse way. Gelatin reduces the rate of dissolution of chromium in the acid; additions of acetic acid act similarly. E. Beutel and A. Kutzelnigg studied the films produced by a boiling soln. of **sodium thiosulphate** and lead acetate. M. G. Levi and co-workers found that a soln. of **potassium persulphate** rapidly dissolves chromium as chromic acid, and a little gas is evolved; the process of dissolution is slow with a soln. of **ammonium persulphate.**

A. Binet du Jassonneix, I. Zschukoff, and J. Férée found when pyrophoric chromium unites with **nitrogen,** a bronze-coloured nitride is formed. F. Adcock found that molten chromium rapidly absorbs nitrogen up to the extent of 3·9 per cent., and G. Valensi, and R. Blix also obtained evidence of the formation of a nitride when nitrogen is absorbed by chromium at an elevated temp. E. Martin studied the occlusion of nitrogen and the formation of nitrides by chromium; G. Tammann suggested complexes are formed under these conditions rather than ordinary compounds—*e.g.* $Cr_4(N_2)$, and $Cr_2(N_2)$. G. G. Henderson and J. C. Gallety observed that at 850° **ammonia** reacts with chromium forming the nitride. W. Guertler and T. Liepus observed that no reaction with 10, 50, and 70 per cent. ammonia soln. occurs in 48 hrs.; and D. F. McFarland and O. E. Harder, that a normal soln. dissolves 1·60 mgrms. per sq. in. per week. F. W. Bergstrom found that **potassamide** in liquid ammonia soln. acts very slowly or not at all on chromium. J. Férée, and F. Emich said that at ordinary temp. pyrophoric chromium unites with **nitric oxide** with incandescence forming a mixture of chromium oxide and nitride. E. Müller and H. Barck observed that nitric oxide has no action on chromium at 600°. A. L. Bernoulli said that nitric oxide is absorbed by chromium, and when the metal is treated with **nitric acid,** and thoroughly washed, it liberates a measurable amount of nitric oxide when allowed to remain in water for several hrs.—active chromium does not yield the gas under similar conditions. W. Rohn found that 10 per cent. nitric acid dissolves 0·013 grm. per sq. dm. per 24 hrs. in the cold, and none in an hour when hot; W. Guertler and T. Liepus observed no action in 48 hrs. with 10 and 50 per cent. nitric acid, or with aqua regia; and D. F. McFarland and O. E. Harder found that normal nitric acid dissolves 0·35 mgrm. per sq. in. per week. W. Hittorf said that nitric acid makes chromium passive. F. Wöhler, E. Jäger and G. Krüss, H. St. C. Deville, and C. C. Palit and N. R. Dhar said that dil. or conc. nitric acid does not act on chromium. H. Moissan said that chromium is very slowly attacked by dil. nitric acid; and that fuming nitric acid, as well as aqua regia, have no action on the metal. E. Frémy, and J. J. Berzelius also noted the resistance the metal offers to attack by aqua regia. A. Granger observed that chromium is attacked by **phosphorus** at 900°. W. Hittorf found that **phosphoric acid** makes chromium passive. W. Rohn found that 10 per cent. phosphoric acid dissolves no chromium in 24 hrs. when cold, or in an hour when hot. He also found that 10 per cent. **acetic acid** dissolves 0·13 grm. per sq. dm. per 24 hrs. in the cold, and 0·03 grm. per sq. dm. per hr. when hot.

According to H. Moissan, chromium reacts with **carbon** when strongly heated, forming a carbide; the chromium also undergoes a process of concentration as in the case of iron. The reaction between carbon and chromium was studied by K. Nischk, R. Kraiczek and F. Sauerwald, and E. Tiede and E. Birnbräuer. G. Charpy said that **carbon monoxide** reacts with chromium at 1000°, forming a mixture of carbon and chromic oxide. H. Moissan also found that at 1200° a mixture of carbon monoxide and **carbon dioxide** attacks chromium superficially, and the metal acquires a crust of chromic oxide mixed with carbon. Hence, the impossibility of obtaining chromium free from carbon in an ordinary metallurgical furnace, even when using crucibles of quicklime. Chromium is oxidized when heated in carbon monoxide. S. Medsforth studied the promotor action of chromium on nickel as catalyst in the hydrogenation of carbon monoxide or dioxide. W. Guertler and T. Liepus observed no action after 4 weeks' exposure to water sat. with carbon dioxide. W. Hittorf said that **citric acid** makes chromium passive; and a similar result was obtained with **formic, acetic, and tartaric acids.** S. Hakomori studied the action of chromium on ammonia in the presence of tartaric acid and glycerol. J. H. Mathews observed that a soln. of **trichloractic acid** in nitrobenzene does not attack chromium. W. Guertler and T. Liepus observed no reaction with citric and tartaric acids during 24 hrs.' exposure. D. F. McFarland and O. E. Harder observed that fatty acids dissolved 1·23 mgrms. per sq. in. per week; and C. B. Gates, that chromium is not attacked by **oleic acid** at room temp. J. G. Thompson and co-workers studied the action of soln. of **urea,** and of **ammonium carbonate** on the metal. H. S. Taylor and G. B. Kistiakowsky discussed chromic oxide as a methanol catalyst; and O. Schmidt as a hydrogenation catalyst. H. Moissan found that when heated in an electric furnace chromium readily unites with **silicon,** forming a silicide; and with **boron,** forming a boride. E. Vigouroux found that at 1200° chromium reacts with **silicon tetrachloride,** forming a silicide; and, according to W. Treitschke and G. Tammann, it attacks **porcelain** vigorously at 1600°.

A. Burger said that the vapour of **calcium** has no appreciable action on chromium at a red-heat. W. G. Imhoff found that chromium resists attack by molten **zinc** more readily than does iron or steel. W. Treitschke and G. Tammann found that the action on **magnesia** at 1700° is quite small. H. Moissan said that fused **potassium hydroxide** has no appreciable action on chromium at dull redness; but J. J. Berzelius said that at a red-heat, in air, the chromium is attacked. W. Guertler and T. Liepus observed no reaction with 10 and 50 per cent. soln. of **sodium hydroxide** during 8 hrs.' exposure. M. Leblanc and O. Weyl found that potassium hydroxide between 550° and 660° has a slight action on chromium, forming traces of potassium and hydrogen. D. F. McFarland and O. E. Harder observed that normal sodium hydroxide dissolves 0·35 mgrm. per sq. in. per week, and normal **sodium chloride,** 2·00 mgrms. per sq. in. per week. U. Sborgi and G. Cappon found that in a soln. of **calcium and ammonium nitrate** in ethyl alcohol, chromium is passive with low current pressures, and with high pressures, chromous ions are formed. J. J. Berzelius, F. Wöhler, and H. Moissan observed that chromium is energetically attacked by fused **potassium nitrate** at a dull red-heat; and that the attack by fused **potassium chlorate** is even more vigorous—the chromium floats on the chlorate producing vivid incandescence. H. Moissan said that chromium is slowly attacked by **mercuric chloride;** W. Guertler and T. Liepus observed a slight action with a 1 : 500 soln. at 90°; and no action with **magnesium chloride** soln.

Some reactions of analytical interest.—Chromic salts give no precipitate with **hydrochloric acid;** and **hydrogen sulphide** gives no precipitate in acidic soln., but in alkaline soln. **ammonium sulphide** precipitates chromic hydroxide; and a similar precipitate is obtained with **ammonia.** According to F. Jackson,[2] the reaction with ammonia is sensitive to 1 : 4000; and with ammonium sulphide to 1 : 8000. The chromic hydroxide is slightly soluble in an excess of ammonia forming a violet soln. The precipitation should be made from a boiling soln. using as little ammonia as possible. Aq. soln. of the **alkali hydroxides** also precipitate chromic hydroxide, and with an excess of the alkali, some chromium passes into soln.: $3KOH+Cr(OH)_3\rightleftharpoons 3H_2O+Cr(OK)_3$, an excess of water or boiling makes the reaction pass from right to left, and unlike the corresponding case with aluminium, nearly all the chromium is precipitated as hydroxide. **Alkali carbonates** also precipitate chromic hydroxide; and similarly J. N. von Fuchs found that **calcium carbonate** precipitates a green chromic carbonate; and H. Demarçay obtained a similar result with **strontium, barium, and magnesium carbonates.** H. Rose said that with cold soln. barium carbonate slowly precipitates green hydrated chromic oxide. A boiling soln. treated with **sodium thiosulphate** gives a precipitate of chromic hydroxide. With **alkali phosphates,** a green precipitate of chromic phosphate is formed; this is soluble in mineral acids and in cold acetic acid; when the acetic acid soln. is boiled, chromic phosphate is again precipitated. **Alkali acetates** give no precipitate with cold or boiling soln., but if aluminium and ferric salts are present in excess, basic acetate is precipitated; if the chromic salt be in excess, the precipitation is incomplete. **Peroxides**—*e.g.* hydrogen, sodium or lead dioxide—and **per-salts**—*e.g.* persulphates, perborates, and percarbonates—convert alkaline soln. into yellow chromates; similarly, **potassium permanganate** in hot, alkaline soln. converts the chromic salt into a chromate. When chromic oxide or hydroxide is fused with alkalies and other bases, in air, chromate is formed.

A yellow soln. of the chromate becomes orange coloured when treated with dil. **sulphuric acid;** and with conc. sulphuric acid, red needles of chromic acid may be formed, and the soln. may become green with the evolution of oxygen: $2CrO_3+3H_2SO_4=3H_2O+3O+Cr_2(SO_4)_3$. In neutral soln., **silver nitrate** gives a brownish-red precipitate soluble in ammonia and mineral acids; with conc. soln. of potassium dichromate, silver nitrate may precipitate reddish-brown silver dichromate which when boiled with water forms a soln. of chromic acid, and normal silver chromate. With **lead acetate,** lead chromate is precipitated; the precipitation is incomplete with lead nitrate unless the soln. contains acetates. According to P. Harting, a precipitate is obtained with lead salts and potassium dichromate and the reaction is sensitive to 1 : 111,982; T. G. Wormley gave 1 : 107,700; and F. Jackson, to 1 : 32,000. Neutral chromates give yellow barium chromate when treated with **barium chloride;** the precipitate is soluble in mineral acids, and insoluble in acetic acid. If dichromates are used the precipitation is incomplete except in the presence of alkali acetates. According to F. Jackson, the reaction with barium salt and potassium dichromate is sensitive to 1 : 256,000. A cold soln. of a chromate gives brown mercurous chromate when treated with **mercurous nitrate;** and if the soln. is boiled, fiery-red, normal mercurous chromate is formed. **Reducing agents**—*e.g.* hydrogen sulphide, sulphur dioxide, etc.—convert the chromates into green chromic salts. According to P. Cazeneuve,[3] N. M. Stover, and A. Moulin, chromates give a purple, violet, red or brown coloration with **diphenylcarbazide,** or the acetate, in alcoholic soln. According to K. Pander, and J. Froidevaux, **guaiacum tincture** gives an evanescent, blue coloration with chromates. J. Meyerfeld obtained a yellowish-red coloration with an aq. soln. of **pyrogallol dimethyl ether;** and P. N. van Eck obtained a blue coloration with an aq. soln. of **α-naphthylamine** and tartaric acid; D. Lindo, a brown band with **phenol,** and a rainbow band with **orcinol;** P. König obtained a red or violet coloration with **1 : 8 dihydroxynaphthalene-3 : 6-disulphonate**—it is said to be sensitive to 0·0000008 grm. of chromium in 10 c.c. L. C. A. Barreswil found that if an acidic soln. of a chromate be treated with **hydrogen dioxide** and then shaken with ether, the upper ethereal layer will be coloured blue—*vide infra,* perchromates. S. N. Chakrabarty and S. Dutt studied organic syntheses with chromium powder.

The physiological action of chromium salts.—According to G. C. Gmelin,[4] chromic chloride is less active than normal potassium chromate; 1·9 grms. of the latter killed a rabbit within 2 hrs., while 3 grms. of the chloride had no action. Subcutaneous injections of 0·2 to 0·4 grm. of potassium chromate were found by E. Gergens, and C. Posner to act with great intensity on rabbits, and death often occurred within a few hours. E. V. Pelikan found that 0·06 to 0·36 grm. of potassium dichromate is fatal to rabbits and dogs. Workmen exposed to the dust of potassium dichromate were stated by B. W. Richardson to acquire a bitter disagreeable taste in the mouth with an increase of saliva which helps to get rid of most of the poison, and little ill-effects are observed. Those who inspire by the nose suffer from inflammation of the septum, which gradually gets thin, then ulcerated, and finally the whole septum is destroyed. The dichromate also causes painful skin eruptions, and ulcerations which the workmen call *chrome holes.* These skin diseases start from an excoriation; so long as the skin remains whole, there is little local effect.

Horses, also, about the works develop ulcerations if the salt get into wounds or cracks in the legs; and the animals may lose their hoofs. Cases of poisoning by chromates are rare. They have been recorded by J. Maschka, E. O. MacNiven, W. A. McLachlan, J. J. Bloomfield and W. Blum, A. M'Crorie, G. Wilson, J. T. Gadsby, A. D. Walker, G. Leopold, O. von Linstow, and R. C. Smith. The symptoms are severe gastro-intestinal inflammation, accompanied by depression, stupor, and death. The subject was discussed by A. Hébert, H. Becker, L. Lewin, etc. The objectionable uses of chromates for preserving milk, etc., was discussed by G. Denigès,[5] and J. Froidevaux; the antiseptic action of chromates by A. Müller, P. Miquel, C. Chamberland and E. Roux, P. J. Laujorrois, J. F. Clark, C. H. Pander, A. Strubell, H. Schulz, H. Coupin, etc. M. E. Pozzi-Escot found that chromic salts are less poisonous than potassium chromate and dichromate, chrome-alum or chromic acid towards the lower fungi—*e.g. saccharomycetes*. P. König found that with certain minute concentrations plant life may be stimulated by chromium salts and chromates; the toxic action is greater the higher the degree of oxidation of the chromium. A wheat plant was killed by a 0·0064 per cent. soln. of sodium dichromate, and a 0·5 per cent. soln. of chrome-alum was needed to produce a similar result. T. Pfeiffer and co-workers could not find any beneficial stimulating effect of chromite, or of potassium dichromate on the growth of oats and barley.

Some uses of chromium.—One of the most important applications of chromium is in the production of various alloys,[6] principally ferrochromium alloys for the manufacture of special steels many of which contain about 2 per cent. of chromium and a small proportion of other metals—*vide* the alloys of iron. The chrome-alloy steels are hard and tough. They are used in making armour-plate, armour-piercing projectiles, burglar-proof safes; tyres, axles, springs for railways and motor-cars, stamp-mill shoes, crusher jaws, the so-called rustless cutlery, *stellite*—an alloy containing chromium, cobalt, and molybdenum and tungsten—for high speed tools which retain their cutting edge at temp. approaching redness; *nichrome*—nickel, chromium, iron (60 : 14 : 15), a high temp. resistance alloy; chromium-vanadium steel; chromium magnet steel; heat-resisting and acid-resisting steels; etc. Chromium plating as a protective coating for steel is much employed [7]—*vide supra*, the electrodeposition of chromium. Perhaps the largest demand for chromium is in the form of chromite used as a refractory in certain parts of open-hearth and other furnaces.[8] Chromium compounds are used in tanning certain leathers—chrome leathers; as a mordant for dyeing; it is used for impregnating wood, paper, etc., with chromic hydroxide; and in the preparation of filaments for incandescent lamps. Chromates are used for making gelatine insoluble—for a mixture of gelatine and potassium dichromate becomes insoluble when exposed to light—in colour printing, block printing, heliography, photolithography, photozincography, etc. Chromium compounds are used in making safety matches; as antiseptics; in bleaching oils; in the purification of wood vinegar; as a component of certain galvanic cells; an oxidation agent in the preparation of some aniline dyes and in a number of analytical and chemical processes; as a catalytic agent in the preparation of sulphur trioxide (*q.v.*), and, according to H. W. Underwood,[9] in the hydrogenation of organic compounds.

Chromic oxide is employed as green pigments for paints—chrome-green, emerald-green, Cassal's green, etc.—and it may be associated with other substances—*e.g.* boric oxide, phosphoric oxide, zinc oxide, etc. to produce special tints, there are yellow chromates of lead, etc.—*e.g.* chrome yellow, lemon yellow, Paris yellow, royal yellow, etc.; red basic lead chromates—*e.g.* chrome-orange, chrome-vermilion, etc.; and brown, manganese chromate.[10] Chromic oxide is employed in producing on-, in-, and underglaze green colours in enamel, pottery and glass manufacture; on-glaze yellows employed for on-glaze work, and in enamelling are derived from lead chromate, the on-glaze reds and orange colours, from basic lead chromate. A crimson or pink colour for pottery decoration is based on the result of calcining stannic oxide with one or two per cent. of chromic oxide; for the coloration of alumina with chromium to form artificial rubies—*vide* alumina. C. J. Smithells[11] described the manufacture of articles from chromium.

REFERENCES.

[1] H. P. Walmsley, *Phil. Mag.*, (7), **7**. 1097, 1929; F. W. Bergstrom, *Journ. Amer. Chem. Soc.*, **47**. 1836, 1925; N. Domanicky, *Journ. Russ. Phys. Chem. Soc.*, **48**. 724, 1916; H. W. Underwood, *Chem. Met. Engg.*, **29**. 709, 1923; H. V. Regnault, *Ann. Chim. Phys.*, (2), **62**. 357, 1836; E. M. Péligot, *ib.*, (3), **12**. 548, 1844; S. Medsforth, *Journ. Chem. Soc.*, **123**. 1452, 1923; F. Adcock, *Journ. Iron Steel Inst.*, **114**. ii, 117, 1926; W. Rohn, *Zeit. Metallkunde*, **18**. 387, 1926; W. Guertler and T. Liepus, *ib.*, **17**. 310, 1925; C. E. Ufer, *Liebig's Ann.*, **112**. 302, 1859; F. Wöhler, *ib.*, **111**. 230, 1859; J. J. Berzelius, *ib.*, **49**. 247, 1844; T. Weichselfelder and B. Thiede, *ib.*, **447**. 64, 1926; B. Thiede, *Ueber die Hydride der Metalle Nickel, Cobalt, Eisen, Chrom*, Berlin, 1926; K. Nischk, *Zeit. Elektrochem.*, **29**. 373, 1923; H. Gruber, *ib.*, **30**. 396, 1924; H. R. Carveth and B. E. Curry, *Journ. Phys. Chem.*, **9**. 353, 1905; C. C. Palit and N. R. Dhar, *ib.*, **30**. 1125, 1926; F. Emich, *Monatsh.*, **15**. 375, 1894; L. N. Vauquelin, *ib.*, **45**. 393, 1794; **46**. 152, 311, 1798; *Journ. Mines*, **6**. 737, 1797; *Nicholson's Journ.*, **2**. 387, 441, 1799; *Phil. Mag.*, **1**. 279, 361, 1798; **2**. 274, 1798; *Ann. Chim. Phys.*, (1), **25**. 21, 194, 1798; F. Fischer and F. Schrötter. *Ber.*, **43**. 1442, 1454, 1910; H. Moissan, *Bull. Soc. Chim.*, (3), **35**. 947, 1906; *Le four électrique*, Paris, 1900; London, 146, 1904; *Compt. Rend.*, **142**. 428, 1906; W. Hittorf, *Sitzber. Akad. München*, **71**. 193, 1898; *Zeit. Elektrochem.*, **6**. 6, 1899; *Zeit. phys. Chem.*, **25**. 729, 1898; **30**. 481, 1899; **34**. 385, 1900; R. Hanslian, *Molekulargewichtsbestimmungen in gefrierendem und siedendem Jod*, Weida a. Th., 1910; A. Gotta, *Ueber die Eigenschaften einiger Metallwasserstoffe*, Leipzig, 1928; D. F. McFarland and O. E. Harder, *Bull. Eng. Univ. Illinois*, 93, 1912; E. H. Harvey, *Chem. Met. Engg.*, **35**. 684, 1928; E. Martin, *Arch. Eisenhüttenwesen*, **3**. 407, 1929; *Stahl Eisen*, **49**. 1861, 1929; *Ein Beitrag zur Frage der Aufnahmefähigkeit des reinen Eisens und einiger seiner Legierungselemente für Wasserstoff und Stickstoff*, Düsseldorf, 1929; A. Binet du Jassonneix, *Compt. Rend.*, **143**. 897, 1906; E. Vigouroux, *ib.*, **144**. 83, 1907; E. Frémy, *ib.*, **44**. 633, 1857; C. Poulenc, *ib.*, **116**. 253, 1893; *Ann. Chim. Phys.*, (7), **2**. 60, 1894; H. St. C. Deville, *ib.*, (3), **46**. 182, 1856; *Compt. Rend.*, **44**. 676, 1857; J. Férée, *ib.*, **121**. 822, 1895; C. Matignon and G. Desplantes, *ib.*, **140**. 853, 1905; G. Charpy, *ib.*, **148**. 560, 1907; A. Granger, *ib.*, **124**. 190, 1897; *Ann. Chim. Phys.*, (7), **14**. 38, 1898; E. Jäger and G. Krüss, *Ber.*, **22**. 2052, 1889; M. Leblanc and O. Weyl, *ib.*, **45**. 2300, 1912; M. G. Levi, E. Migliorini and G. Ercolini, *Gazz. Chim. Ital.*, **38**. i, 583, 1908; C. F. Hüttig, *Zeit. angew. Chem.*, **39**. 67, 1926; F. W. Brodkorb, *Zur Kenntnis der Verbindungen des Wasserstoffs mit den Metallen Calcium, Natrium, Kupfer und Chrom*, Leipzig, 1927; G. F. Hüttig and F. W. Brodkorb, *Zeit. anorg. Chem.*, **144**. 341, 1925; C. F. Hüttig, *ib.*, **153**. 235, 1926; A. Sieverts and A. Gotta, *ib.*, **172**. 1, 1928; G. Tammann, *Nachr. Gött.*, 225, 1919; *Zeit. anorg. Chem.*, **188**. 396, 1930; W. Treitschke and G. Tammann, *ib.*, **55**. 402, 1907; W. Biltz, *ib.*, **174**. 42, 1928; E. Müller and H. Barck, *ib.*, **129**. 309, 1923; E. Tiede and E. Birnbräuer, *ib.*, **87**. 129, 1914; T. Döring, *Journ. prakt. Chem.*, (2), **66**. 65, 1902; I. Zschukoff, *Ann. Inst. Anal. Phys. Chem.*, **3**. 14, 1926; A. L. Bernoulli, *Die Passivität des Chroms nach der Faradayschen Theorie*, München, 1904; *Phys. Zeit.*, **5**. 632, 1904; S. Hakomori, *Science Rep. Tohoku Univ.*, **16**. 841, 1927; R. Blix, *Zeit. phys. Chem.*, **3**. B, 229, 1929; G. G. Henderson and J. C. Galletly, *Journ. Soc. Chem. Ind.*, **27**. 387, 1908; J. Voisin, *Rev. Mét.*, **7**. 1146, 1910; J. H. Mathews, *Journ. Phys. Chem.*, **9**. 659, 1905; W. G. Mixter, *Amer. Journ. Science*, (4), **26**. 125, 1908; A. Burger, *Ber.*, **39**. 4068, 1906; *Reduktion durch Calcium*, Basel, 1907; N. B. Pilling and R. E. Bedworth, *Metal Ind.*, **22**. 560, 1923; *Journ. Inst. Metals*, **29**. 529, 1923; H. S. Taylor and G. B. Kistiakowsky, *Journ. Amer. Chem. Soc.*, **49**. 2468, 1927; O. Schmidt, *Zeit. phys. Chem.*, **113**. 193, 1925; L. J. Thénard, *Traité de chimie*, **2**. 68, 1824; G. Valensi, *Journ. Chim. Phys.*, **26**. 152, 1929; W. G. Imhoff, *Amer. Metal Market*, **37**. 106, 1930; J. G. Thompson, H. J. Krause and K. G. Clark, *Journ Ind. Eng. Chem.*, **22**. 735, 1930; C. B. Gates, *Journ. Phys. Chem.*, **15**. 97, 1911; R. Kraiczek and F. Sauerwald, *Zeit. anorg. Chem.*, **185**. 193, 1929; E. Beutel and A. Kutzelnigg, *Zeit. Elektrochem.*, **36**. 523, 1930; G. Walpert, *Zeit. phys. Chem.*, **151**. 219, 1930; U. Sborgi and G. Cappon, *Nuovo Cimento*, (6), **23**. 303, 1922; H. Moissan, *Ann. Chim. Phys.*, (5), **21**. 253, 1880.

[2] J. N. von Fuchs, *Schweigger's Journ.*, **62**. 191, 1831; H. Demarçay, *Liebig's Ann.*, **11**. 241, 1834; H. Rose, *Pogg. Ann.*, **83**. 143, 1851; F. Jackson, *Journ. Amer. Chem. Soc.*, **25**. 992, 1903; P. Harting, *Bull. Sciences Néerl.*, **2**. 164, 1841; *Journ. prakt. Chem.*, (1), **22**. 52, 1841; T. G. Wormley, *Microchemistry of Poisons*, New York, 1879.

[3] P. Cazeneuve, *Journ. Pharm. Chim.*, (6), **12**. 150, 1900; *Compt. Rend.*, **131**. 346, 1900; *Bull. Soc. Chim.*, (3), **25**. 761, 1901; A. Moulin, *ib.*, (3), **31**. 295, 1904; S. N. Chakrabarty and S. Dutt, *Journ. Indian Chem. Soc.*, **5**. 513, 1928; J. Meyerfeld, *Chem. Ztg.*, **34**. 948, 1910; P. König, *ib.*, **35**. 277, 1911; P. N. van Eck, *Chem. Weekbl.*, **12**. 6, 1915; K. Pander, *Arb. Pharm. Inst. Dorpat.*, **2**. 1, 1888; *Berlin. Klin. Wochensschr.*, **25**. 835, 1888; J. Froidevaux, *Journ. Pharm. Chim.*, (5), **4**. 155, 1896; D. Lindo, *Chem. News*, **58**. 28, 1888; L. C. A. Barreswil, *Compt. Rend.*, **16**. 1885, 1847; *Ann. Chim. Phys.*, (3), **20**. 364, 1848; N. M. Stover, *Journ. Amer. Chem., Soc.*, **50**. 2363, 1928.

[4] G. C. Gmelin, *Versuche über die Wirkungen des Baryts, Strontians, Chroms, Molybdäns,*

Wolframs, Tellurs, Titans, Osmiums, Platins, Iridiums, Rhodiums, Palladiums, Nickels, Kobalts, Urans, Ceriums, Eisens, und Mangans auf den thierischen Organisms, Tubingen, 1924 ; *Schweigger's Journ.*, **43**. 110, 1823 ; *Edin. Met. Journ.*, **3**. 324, 1827 ; E. Gergens, *Arch. exp. Path. Pharmakol.*, **6**. 148, 1876 ; C. Posner, *Virchow's Arch.*, **79**. 311, 1880 ; E. V. Pelikan, *Beiträge zur gerichtlichen Medicin, Toxikologie, und Pharmakoll.*, Würzburg, 1858 ; B. W. Richardson, *Brit. Foreign Med. Chirurg. Rev.*, **32**. 533, 1863 ; J. J. Bloomfield and W. Blum, *Health Hazards in Chromium Plating*, Washington, 1928 ; R. C. Smith, *Lancet*, i, 391, 1882 ; E. O. MacNiven, *ib.*, ii, 496, 1883 ; J. T. Gadsby, *ib.*, i, 167, 1880 ; A. D. Walker, *ib.*, ii, 464, 1879 ; W. A. McLachlan, *Glasgow Med. Journ.*, **16**. 31, 1881 ; A. M'Crorie, *ib.*, **15**. 378, 1881 ; G. Wilson, *Med. Gaz.* (*London*), **33**. 734, 1844 ; G. Leopold, *Viertelj. ger. Med.*, **27**. 29, 1877 ; O. von Linstow, *ib.*, **20**. 60, 1874 ; J. Maschka, *Prag. Viertelj. prakt. Heilk.*, **131**. 37, 1877 ; *Handbuch der gerichtlichen Medicin*, Tübingen, **2**. 3, 1882 ; A. W. and M. W. Blyth, *Poisons*, London, 701, 1906 ; A. Hébert, *Bull. Soc. Chim.*, (4), **1**. 1026, 1907 ; *Compt. Rend.*, **145**. 337, 1907 ; H. Becker, *Collegium*, 35, 1906 ; L. Lewin, *Chem. Ztg.*, **31**. 1076, 1907 ; A. T. E. Wutzdorff, *Arb. Kaiser. Ges. Amt.*, **13**. 328, 1897.

[5] C. Chamberland, *Ann. Pasteur. Inst.*, **1**. 153, 1887 ; *Journ. Pharm. Chim.*, (5), **16**. 126, 1887 ; C. Chamberland and E. Roux, *Compt. Rend.*, **96**. 1088, 1883 ; H. Coupin, *ib.*, **127**. 977, 1898 ; C. H. Pander, *Centr. Baktenol.*, **25**. 835, 1888 ; M. E. Pozzi-Escot, *Bull. Assoc. Chim. Sucre Dist.*, **21**. 1141, 1904 ; H. Schulz, *Biedermann's Centr.*, **17**. 485, 1888 ; T. Pfeiffer, W. Simmermacher and A. Rippel, *ib.*, **49**. 259, 1920 ; *Fuhling's Landw. Zeit.*, **17**. 313, 1918 ; J. Froidevaux, *Journ. Pharm. Chim.*, (6), **4**. 155, 1896 ; G. Denigès, *Rev. Falsif. Internat.*, **9**. 36, 1897 ; A. Strubell, *Dingler's Journ.*, **272**. 129, 1889 ; P. J. Laujorrois, *Union Pharm.*, **25**. 19, 1884 ; *Arch. Pharm.*, (3), **22**. 427, 1884 ; A. Müller, *Landw. Vers.*, **32**. 271, 1885 ; P. Miquel, *Monit. Scient.*, (3), **14**. 170, 1884 ; J. F. Clark, *Journ. Phys. Chem.*, **3**. 306, 1899 ; P. König, *Chem. Ztg.*, **35**. 205, 1911 ; *Landw. Jahr.*, **39**. 775, 1910.

[6] U. Coppa, *Rass. Min. Met. Chim.*, **55**. 111, 1922 ; Anon., *Metal Ind.*, **31**. 98, 1924 ; C. B. Bellis, *Chem. Met. Engg.*, **30**. 149, 1924 ; G. C. Fink, *Journ. Soc. Autom. Eng.*, **20**. 157, 1927.

[7] G. C. Fink, *Blast Furnace and Steel Plant*, **13**. 234, 1925 ; S. Wernick, *Nature*, **120**. 225, 1927 ; H. C. H. Carpenter, *ib.*, **120**. 225, 1927.

[8] E. G. von Odelstjerna, *Jern. Kontorets Ann.*, (2), **43**. 378, 1888 ; *Dingler's Journ.*, **272**. 65, 1889 ; *Stahl Eisen*, **8**. 873, 1888 ; J. Bach, *German Pat.*, *D.R.P.* 154750, 158268, 1903 ; R. Tripmacher, *ib.*, 230033, 1909 ; M. Reiche, *ib.*, 205883, 1907 ; M. Simonis, *Stahl Eisen*, **28**. 334, 1908 ; J. W. Furness, *Metal Ind.*, **31**. 151, 1927.

[9] H. W. Underwood, *Chem. Met. Engg.*, **29**. 709, 1923.

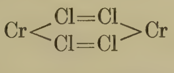
[10] C. F. Binns and E. Craig, *Journ. Amer. Cer. Soc.*, **10**. 73, 1927.

[11] C. J. Smithells, *Brit. Pat. No.* 285571, 1926.

§ 6. The Atomic Weight and Valency of Chromium

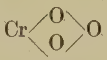
In 1818, J. J. Berzelius[1] represented chromic anhydride by the formula CrO_6 but later gave CrO_3, and the corresponding formula for chromic oxide became Cr_2O_3 by analogy with the sesquioxides of aluminium, iron and manganese. This made the at. wt. of chromium approximate to 52, and is in agreement with the tervalency of chromium in this oxide, and also with the sp. ht. rule ; with the isomorphism of the chromous and ferrous salts observed by C. Laurent ; the isomorphic replacement of chromic, ferric, and aluminium hydroxides in the silicate minerals, spinels and chromites, alums, and complex cyanides ; and the isomorphism of chromates and sulphates—*vide supra*. The at. wt. 52 also agrees with the electrolysis of chromium salts which is in accord with Faraday's law ; with the recognized position of chromium in the periodic table ; and with the frequency of the X-rays observed by H. G. J. Moseley, and M. Siegbahn and W. Stenström.

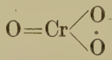
Chromium under different conditions may act as a bi-, ter-, and sexi-valent element. F. Pintus discussed the possibility of the formation of compounds with *univalent* chromium in such reactions as : $4CrCl_2+4C_6H_5MgBr=(C_6H_5)_4CrCl+3CrCl\ 2MgCl_2+2MgBr_2$. *Bivalent* chromium in the dichloride has a vap. density at 1600° half as much again too high for the simple molecule $CrCl_2$, and, according to L. F. Nilson and O. Pettersson, the chromium is really tervalent $Cr_2{=}Cr{-}Cr{=}Cl_2$; but it may be

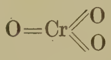


$$Cr{<}\begin{smallmatrix}Cl=Cl\\Cl=Cl\end{smallmatrix}{>}Cr$$

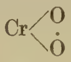
The isomorphism between $CrSO_4.7H_2O$, and $FeSO_4.7H_2O$, indicated by C. Laurent, shows that the bivalency of chromous chromium corresponds with the bivalency of ferrous iron. The *tervalency* of chromium has been more definitely established by L. F. Nilson and O. Pettersson's observations on the vap. density of chromic chloride ; F. Hein and E. Markert's observations on triphenyl chromium, $Cr(C_6H_5)_3$; and G. Urbain and A. Debierne's observations on the vap. density of chromic acetylacetonate. There is also the isomorphism of chromium with tervalent aluminium in the alums. W. Just, W. Eissner, E. Markert, and F. Hein and co-workers also prepared tetraphenyl chromium, $Cr(C_6H_5)_4$, in which the metal is presumably *quadrivalent ;* and possibly *quinquevalent* in the compounds of the type $Cr(C_6H_5)_4OH$. The *sexivalency* of chromium is indicated by F. Hein's observations on the vap. density of chromyl chloride ; and by the relations between sulphur trioxide, SO_3, and chromic trioxide, CrO_3, as illustrated by the isomorphism of the sulphates and chromates observed by E. Mitscherlich, F. Mylius and R. Funk, and H. Salkowsky. Of course, chromium, in chromic anhydride, may be bi- or quadri-valent


Bivalent.

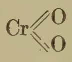

Quadrivalent.


Sexivalent.

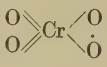
and W. Manchot believed that the chromium is quadri- not sexi-valent, and similarly also with the other cases of sexivalent chromium ; hence, the whole force of the argument turns on the analogy with what he assumed to be sexivalent sulphur. W. Manchot and R. Kraus reported chromium dioxide, CrO_2, in which the chromium is bi-, ter-, or quadrivalent

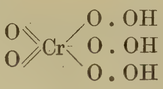

Bivalent.

O=Cr–O–O–Cr=O
Tervalent.


Quadrivalent.

and W. Manchot believed it to be *quadrivalent.* The isomorphism of the complex salts of chromium oxytrichloride, $CrOCl_3$, say $CrOCl_3.2CsCl$ with $CbOCl_3.2CsCl$, observed by R. F. Weinland and co-workers, agrees with the assumption that chromium is here quinquevalent. F. Olsson obtained addition products of quinquevalent chromium. R. Luther and T. F. Rutter also assumed that in the reaction between hydriodic acid and chromic acid, the chromium is first reduced to a quinquevalent stage and then to a quadrivalent stage. According to E. H. Riesenfeld, chromium in chromium tetroxide, CrO_4, is sexivalent, and in the perchromate H_3CrO_8, *septivalent :*


CrO_4


H_3CrO_8

A. Werner,[2] and P. Pfeiffer and co-workers described optically active chromic diaquodiethylenediamine salts, $[Cren_2(H_2O)_2]X_3$; chromic hydroxyaquodiethylenediamine salts, $[Cren_2(OH)(H_2O)]X_2$; A. Werner, and P. Pfeiffer and co-workers, chromic dichlorodiethylenediamine salts, $[Cren_2Cl_2]X$; chromic dibromodiethylenediamine salts, $[Cren_2Br_2]X$; and chromic dithiocyanatodiethylenediamine salts, $[Cren_2(SCy)_2]X$.

J. J. Berzelius [3] made the first serious determination of the at. wt. of chromium ; he precipitated lead nitrate with an alkali chromate, and weighed the resulting lead chromate. His results for the at. wt. gave 56 from the ratio $Pb(NO_3)_2 : PbCrO_4$; and 54 from $BaCrO_4 : BaSO_4$. Later observers have shown that the method is unreliable—with conc. soln., the precipitate adsorbs alkaline salts, and with dil. soln., the precipitation is incomplete. E. M. Péligot analyzed chromous acetate and chromium chloride, and obtained a value for the at. wt. 52·5, much lower than that of J. J. Berzelius ; and V. A. Jacquelain obtained a very low result, 50·1. In neither case were sufficient data described in the reports to enable estimates to be made of the value of the work. Some general observations on the subject were made by W. A. Noyes, and S. Lupton.

In 1846, N. J. Berlin obtained 52·6 to 52·9 from the ratio $2AgCl : Ag_2CrO_4$; 52·3 to 52·5 from $Cr_2O_3 : 2Ag_2CrO_4$; 52·6 from $2AgCl : Ag_2Cr_2O_7$; 52·3 from $Cr_2O_3 : Ag_2Cr_2O_7$; and 52·0 from $Pb(NO_3)_2 : PbCrO_4$. A. Moberg obtained 53·2 from the ratio $Cr_2O_3 : Cr_2(SO_4)_3$; 53·7 from $Cr_2O_3 : Cr_2(SO_4)_3$; and 53·6 from Cr_2O_3 : chrome-alum. J. Lefort calculated 53·1 from the ratio $BaCrO_4 : BaSO_4$; and R. Wildenstein, 53·6 from $BaCrO_4 : BaCl_2$. F. Kessler obtained 52·2 to 52·4 from the ratio $KClO_3 : K_2Cr_2O_7$; M. Siewert, 52·05, from $CrCl_3 : 3AgCl$; 52·1, from $Ag_2Cr_2O_7 : 2AgCl$; and 52·0, from $Ag_2Cr_2O_7 : Cr_2O_3$; H. Baubigny, 52·1 from $Cr_2(SO_4)_3 : Cr_2O_3$; S. G. Rawson, 52·2 from $(NH_4)_2Cr_2O_7 : Cr_2O_3$; F. W. Meinecke, 52·2, from $(NH_4)_2Cr_2O_7 : Cr_2O_3$; 52·08, from $4AgCl : Cr_2O_3$; 52·06, from $Ag_2CrO_4 : I_2$; 52·2, from $[Ag_2(NH_3)_4]CrO_4 : I_2$; 52·10, from $K_2Cr_2O_7 : KClO_3$; and 52·13, from $(NH_4)_2Cr_2O_7 : I_2$; F. G. Nunez, 52·025, from $CrCl_2O_2 : 2AgCl$; G. P. Baxter, E. Mueller and M. A. Hines, 52·005, from $2AgCl : Ag_2CrO_4$, and 52·012, from $2AgBr : Ag_2CrO_4$; and G. P. Baxter and R. H. Jesse, 52·016, from $2AgBr : Ag_2Cr_2O_7$. J. Meyer gave $52·01 \pm 0·01$ as the best representative value; F. W. Clarke, $52·0193 \pm 0·0013$; while the International Table for 1926 gave 52·01.

The **atomic number** of chromium is 24. F. W. Aston[4] found chromium has four **isotopes** with mass numbers and percentage abundance respectively 50 and 4·9; 52 and 81·6; 53 and 10·4; and 54 and 3·1, making the at. wt. 52·011. N. Bohr gave for the **electronic structure** (2) for the K-shell; (4, 4) for the L-shell; (4, 4, 4) for the M-shell; and (2) for the N-shell. Speculations on the subject were made by S. Meyer, R. H. Ghosh, H. Lessheim and co-workers, C. D. Niven, K. Höjendahl, R. G. W. Norrish, R. Samuel and E. Markowicz, D. M. Bose, F. Hund, I. Tamm, R. Ladenburg, A. S. Russell, P. Ray, J. D. M. Smith, J. N. Frers, O. Feussner, C. G. Bedreag, A. Sommerfeld, and N. Collins. Evidence of **atomic disintegration** by bombardment with α-rays was observed by H. Pettersson and G. Kirsch. The subject was discussed by G. I. Podrowsky.

REFERENCES.

[1] J. J. Berzelius, *Schweigger's Journ.*, **22.** 53, 1818; *Pogg. Ann.*, **8.** 22, 1926; E. Mitscherlich, *ib.*, **18.** 168, 1846; G. Urbain and A. Debierne, *Compt. Rend.*, **129.** 302, 1890; C. Laurent, *ib.*, **131.** 111, 1900; L. F. Nilson and O. Pettersson, *ib.*, **107.** 529, 1888; F. Mylius and R. Funk, *Ber.*, **33.** 3686, 1900; H. Salkowsky, *ib.*, **34.** 1947, 1901; F. Hein, *ib.*, **52.** 195, 1919; H. G. J. Moseley, *Phil. Mag.*, (6), **26.** 1024, 1913; M. Siegbahn and W. Stenström, *Phys. Zeit.*, **17.** 48, 1916; F. Olsson, *Arkiv. Kemi Min. Geol.*, **9.** 10, 1924; E. Carstangen, *Journ. prakt. Chem.*, (2), **2.** 51, 1870; W. Manchot, *Ueber Sauerstoff Activierung*, Würzburg, 1908; *Verh. Phys. Med. Ges. Würzburg*, **39.** 236, 1908; W. Manchot and R. Kraus, *Ber.*, **39.** 3512, 1906; W. Manchot and O. Wilhelms, *Liebig's Ann.*, **325.** 125, 1902; R. F. Weinland and W. Fridrich, *Ber.*, **38.** 3784, 1905; R. F. Weinland and M. Fiederer, *ib.*, **39.** 4042, 1906; **40.** 2090, 1907; E. H. Riesenfeld, *ib.*, **41.** 3536, 1908; R. Luther and T. F. Rutter, *Zeit. anorg. Chem.*, **54.** 1, 1907; F. Hein and E. Markert, *Ber.*, **61.** B, 2255, 1928; E. Markert, *Ueber radikalartige Organometallverbindungen des Chroms*, Leipzig, 1929; W. Eissner, *Weitere Beiträge zur Kenntnis der chromorganischen Verbindungen*, Leipzig, 1926; F. Hein, *Ber.*, **52.** B, 195, 1919; **54.** B, 1938, 2708, 2727, 1921; F. Hein and H. Meininger, *Zeit. anorg. Chem.*, **145.** 95, 1925; H. Meininger, *Ueber metallorganische Basen*, Leipzig, 1924; F. Hein and O. Schwartzkopff, *Ber.*, **57.** B, 8, 1924; F. Hein and R. Spaete, *ib.*, **57.** B, 899, 1924; **59.** B, 751, 1926; W. Just, *Ueber die Bindung von Wasserstoff an Tetraphenylchromsalze und über eine Umkehrung der anormalen Salzbildung des Pentaphenylchromhydroxydes*, Leipzig, 1929; F. Hein, J. Reschke and F. Pintus, *Ber.*, **60.** B, 749, 1927; F. Pintus, *Ueber die Existenz des einwertigen Chroms und den Einfluss der Komplexkonstitution auf die Bildung chromorganischer Verbindungen*, Leipzig, 1928.

[2] P. Pfeiffer, *Zeit. anorg. Chem.*, **56.** 261, 1907; P. Pfeiffer and R. Stein, *ib.*, **58.** 240, 1908; *Ber.*, **40.** 3836, 1907; P. Pfeiffer and R. Prade, *Zeit. anorg. Chem.*, **58.** 249, 1908; P. Pfeiffer and P. Koch, *Ber.*, **37.** 4282, 1904; P. Pfeiffer and T. G. Lando, *ib.*, **37.** 4281, 1904; P. Pfeiffer and A. Trieschmann, *ib.*, **40.** 3837, 1907; *Zeit. anorg. Chem.*, **56.** 283, 1907; A. Werner, *Ber.*, **44.** 1887, 2445, 3132, 3279, 1911; **45.** 433, 1228, 1912.

[3] J. J. Berzelius, *Schweigger's Journ.*, **22.** 53, 1818; *Pogg. Ann.*, **8.** 22, 1826; N. J. Berlin, *Akad. Handl. Stockholm*, 65, 1845; *Journ. prakt. Chem.*, (1), **38.** 145, 1846; (1), **71.** 191, 1857; R. Wildenstein, *ib.*, (1), **59.** 27, 1853; A. Moberg, *ib.*, (1), **43.** 114, 1847; *De oxido chromoso*, Helsingfors, 1847; S. Meyer, *Naturwiss.*, **15.** 623, 1927; E. M. Péligot, *Ann. Chim. Phys.*, (3),

12. 544, 1844; *Compt. Rend.*, **19**. 609, 734, 1844; **20**. 1187, 1845; **21**. 76, 1845: F. Kessler, *Pogg. Ann.*, **95**. 208, 1855; **113**. 139, 1861; M. Siewert, *Zeit. Ges. Naturwiss.*, **17**. 535, 1861; V. A. Jacquelain, *Proc. Verb. Soc. Phil.*, 55, 1847; *Compt. Rend.*, **24**. 674, 1847; H. Baubigny, *ib.*, **98**. 146, 1884; J. Lefort, *ib.*, **30**. 416, 1850; *Journ. Pharm. Chim.*, (3), **18**. 27, 1850; S. Lupton *Proc. Chem. Soc.*, **4**. 81, 1889; *Chem. News*, **58**. 23, 1888; S. G. Rawson, *Journ. Chem. Soc.*, **55**. 213, 1889; F. W. Meinecke, *Liebig's Ann.*, **261**. 339, 1891; W. A. Noyes, *Ber.*, **24**. 238, 1891; F. W. Clarke, *Phil. Mag.*, (5), **12**. 101, 1881; *Amer. Chem. Journ.*, **3**. 268, 1881; *Journ. Amer. Chem. Soc.*, **19**. 359, 1897; *A Recalculation of the Atomic Weights*, Washington, 340, 1910; J. Meyer in R. Abegg, *Handbuch der anorganischen Chemie*, Leipzig, **4**. i (2), 3, 1921; G. P. Baxter and R. H. Jesse, *Zeit. anorg. Chem.*, **62**. 313, 331, 1909; *Journ. Amer. Chem. Soc.*, **31**. 529, 541, 1909; G. P. Baxter, E. Mueller and M. A. Hines, *ib.*, **31**. 529, 1909; *Zeit. anorg. Chem.*, **62**. 313, 1909; G. I. Podrowsky, *Zeit. Physik*, **57**. 560, 1929; C. D. Niven, *Phil. Mag.*, (7), **3**. 1314, 1927; H. Lessheim, J. Meyer and R. Samuel, *Zeit. Physik*, **63**. 299, 1927; F. G. Nunez, *Anal. Fis. Quim.*, **28**. 579, 1930.

[4] F. W. Aston, *Journ. Soc. Chem. Ind.—Chem. Ind.*, **42**. 935, 1923; *Phil. Mag.*, (6), **47**. 399, 1924; (6), **49**. 1191, 1925; *Nature*, **112**. 449, 1923; **126**. 200, 1930; O. Feussner, *Zeit. Physik*, **25**. 215, 1924; D. M. Bose, *ib.*, **35**. 219, 1925; I. Tamm, *ib.*, **32**. 582, 1925; R. Samuel and E. Markowicz, *ib.*, **38**. 22, 1926; F. Hund, *ib.*, **33**. 345, 1925; **34**. 296, 1925; N. Collins, *Chem. News*, **120**. 169, 1920; **129**. 331, 1925; P. Ray, *Zeit. anorg. Chem.*, **174**. 189, 1928; N. Bohr, *Nature*, **112**. Suppl., 1923; A. S. Russell, *ib.*, **115**. 455, 1924; **117**. 47, 1925; R. G. W. Norrish, *Chem. News*, **124**. 16, 1922; H. Pettersson and H. Kirsch, *Atomzertrümmerung*, Leipzig, 1926; *Sitzber. Akad. Wien*, **134**. 431, 1925; R. Ladenburg, *Naturwiss.*, **8**. 5, 1920; S. Meyer, *ib.*, **15**. 623, 1927; A. Sommerfeld, *Ann. Physik*, (4), **70**. 32, 1923; R. H. Ghosh, *Journ. Indian Chem. Soc.*, **4**. 423, 1927; C. G. Bedreag, *Compt. Rend.*, **179**. 768, 1924; **180**. 653, 1925; K. Höjendahl, *Phil. Mag.*, (6), **48**. 349, 1924; C. D. Niven, *ib.*, (7), **3**. 1314, 1927; D. M. Bose, *ib.*, (7), **5**. 1048, 1928; H. Lessheim, J. Meyer and R. Samuel, *Zeit. Physik*, **63**. 299, 1927; G. I. Podrowsky, *ib.*, **57**. 560, 1929; J. D. M. Smith, *Journ. Chem. Soc.*, 2029, 1927; J. N. Frers, *Zeit. anorg. Chem.*, **186**. 145, 1930.

§ 7. The Alloys of Chromium. Chromides

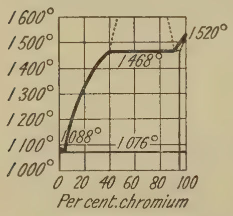


FIG. 7.—Freezing-point Curve of Cu–Cr Alloys.

G. Hindrichs[1] prepared **copper-chromium alloys** by the direct union of the elements. G. Hindrichs said that in the molten state the elements are only slightly soluble in one another; H. Moissan said that molten copper can take up 0·5 per cent. of chromium; and A. B. du Jassonneix that boiling copper can take up 1·6 per cent. of chromium. G. Hindrichs found that the emulsion formed by the two elements does not separate readily into two layers. E. Siedschlag's f.p. curve is shown in Fig. 7. E. Siedschlag found that there is only a partial miscibility in the liquid state with a eutectic at 1076° and 1·5 per cent. of copper. The limits within which a mixture of the two liquids is formed are 37 and 93 per cent. of chromium, above 1470°. Only heterogeneous mixtures of two kinds of crystals are obtained in the solid state, chromium, and a eutectic rich in copper. E. Placet, the Electrometallurgical Co., and D. S. Ashbrook deposited electrolytically a mixture of the two elements. The Neo-Métallurgie Marbeau, and L. P. Hamilton and E. F. Smith heated a mixture of chromium and copper oxides with carbon; P. L. Hulin reduced the mixed oxides with sodium; and H. Goldschmidt, with aluminium. G. Hindrichs reduced a mixture of chromic oxide, potassium dichromate, and cupric sulphide. H. Goldschmidt said that an alloy with 10 per cent. of chromium is greyish-red and harder than copper. L. P. Hamilton and E. F. Smith prepared a greyish-red alloy with 7 per cent. chromium and a sp. gr. 8·346. The Electrometallurgical Co. reported that chromium containing one-thousandth part of copper is harder and tougher than copper; alloys with 0·5 to 20 per cent. of chromium have approximately the toughness of steel, and they are very resistant towards acids, and alkalies, and they also resist high temp. M. G. Corson studied the hardness of the alloys. D. F. McFarland and O. E. Harder observed that the sp. gr. of the alloys with 91·68, 83·02, and 74·05 per cent. of copper were respectively 8·78, 8·60, and 8·47; and Brinell's hardness, respectively <68, 69, and 68. The corrosion of the alloys by normal hydrochloric, sulphuric, and nitric acids, normal soln. of sodium chloride, and hydroxide, ammonium hydroxide and fatty acids, expressed in terms of the loss in mgrms. per sq. in. per week, are indicated in Table II.

TABLE II.—THE CORROSION OF CHROMIUM-COPPER ALLOYS.

Copper (Per cent.).	NaOH.	HCl.	H_2SO_4.	HNO_3.	NaOH.	NH_4OH.	Fatty acids.
91·68	4·33	42·8	17·20	12·60	10·40	41·80	10·50
83·02	4·00	38·3	14·20	13·10	9·6	57·50	—
74·05	4·60	30·3	16·40	60·30	8·86	67·50	10·70

The **silver-chromium alloys** have not been closely studied. According to G. Hindrichs, liquid chromium and silver are only partially miscible; solid soln. are not formed. The addition of 5 per cent. of silver lowers the f.p. of chromium 50°. A reconstructed curve by G. Hindrichs is shown in Fig. 8. L. Jordan and co-workers measured the hardness, tensile strength, and elongation of these alloys. R. Vogel and E. Trilling's observations on the **gold-chromium alloys** are summarized in Fig. 9. No compounds of definite composition are formed. There are three kinds of mixed crystals, one rich in chromium, and two rich in gold. The Greek letters in Fig. 9 refer to the solid soln.

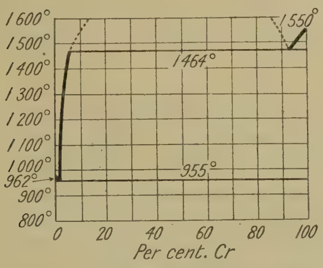


FIG. 8.—Freezing-point Curve of Ag–Cr Alloys.

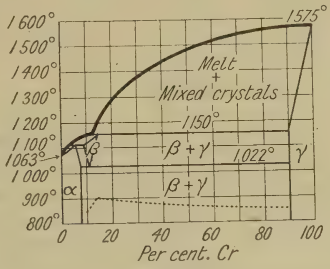


FIG. 9.—Freezing-point Curve of Au–Cr Alloys.

According to H. le Chatelier,[2] a **zinc-chromium alloy,** with 7 per cent. Cr, can be obtained by melting zinc mixed with alkali and chromic chloride. G. Hindrichs found that molten zinc dissolves a little chromium; an alloy with 5 per cent. of chromium had a break 10°–15° above the m.p., and an arrest near the m.p. of zinc. No **cadmium-chromium alloy** could be obtained by heating a mixture of the two elements for 6 hrs. at 650°.

A. S. Russell and co-workers [3] found chromium to be slightly soluble in mercury. G. Tammann and J. Hinnüber said that the solubility of chromium in mercury is $3 \cdot 1 \times 10^{-11}$ per cent. C. F. Schönbein, N. Bunge, Z. Roussin, and C. W. Vincent prepared a **mercury-chromium alloy** or **chromium amalgam,** by the action of potassium or sodium amalgam on a conc. soln. of chromic chloride; and H. Moissan obtained the amalgam by a similar process, as well as by the action of sodium amalgam on chromous chloride, bromide, or iodide. R. Myers obtained it by the electrolysis of a soln. of chromic sulphate in dil. sulphuric acid using a platinum anode, and mercury cathode; J. Férée found that with a soln. of chromic chloride the yield is poor. H. Moissan said that the amalgam is less fluid than mercury; and J. Férée, that it decomposes in air into chromous oxide and mercury. G. Tammann and J. Hinnüber obtained amalgams by reducing soln. of chromium sulphate with a mercury cathode. H. Moissan added that in air, the amalgam acquires a black film of oxide. It is slowly decomposed by dry air, and rapidly in moist air. R. Myers also found that it is rapidly decomposed by water. C. F. Schönbein observed that when the amalgam is shaken with water and air some hydrogen dioxide is formed; this reaction is favoured by dil. sulphuric acid. H. Moissan found that the amalgam is insoluble in boiling, conc. sulphuric acid, and that it is soluble in dil. sulphuric acid. It is soluble in nitric acid, and T. Dieckmann and O. Hauf added that with dil. nitric acid the amalgam forms chromous oxide and mercury. A. S. Russell and co-workers found that the order of removal of metals from mercury amalgam by an oxidizing agent is: Zn, Cd, Mn, Tl, Sn, Pb, Cu, Cr, Fe, Bi, Co, and Ni. According to J. Férée, only dil. amalgams are produced by the action of sodium amalgams on chromic chloride, or by the electrolysis of chromium salts with a mercury cathode; better results are obtained by electrolyzing a soln. containing 160 grms. of chromic chloride and 100 grms. of conc. hydrochloric acid in 740 grms. of water by means of a powerful current with a mercury cathode and a platinum anode. Using a current of 22 ampères and a mercury surface of 8·05 sq. cm. he obtained 1·5 kilo. of a solid chromium amalgam. When dried and filtered through chamois leather, the amalgam has the composition **mercury tritachromide,** Hg_3Cr. When this is subjected to a press. of 200 kgrms. per sq. cm., it loses mercury and yields **mercury monochromide,** HgCr. The first amalgam is soft, brilliant, and alters but little in air, but when heated loses mercury without melting and oxidizes rapidly; the second is brilliant and harder, but alters more readily. When distilled in vacuo below 300°, they both yield chromium which is pyrophoric at ordinary temp. M. Rabinovich and P. B. Zywotinsky observed that chromium can be dispersed in mercury above the solubility limit and so form a colloidal soln.

F. T. Sisco and M. R. Whitmore [4] obtained **aluminium-chromium alloys** with up to 5 per cent. aluminium, by direct fusion of the two elements. G. Hindrichs could not obtain alloys with more than 70 per cent. chromium by heating a mixture of the two elements in an electric furnace. The alloys were obtained by H. Moissan by reducing chromic oxide with aluminium in excess. G. Hindrichs said that the best mode of preparing the alloys is by igniting a mixture of aluminium, chromic oxide, and potassium dichromate. C. Combes obtained crystalline alloys by the action of the vapour of chromic chloride on aluminium; F. Wöhler obtained the alloys by fusing a mixture of aluminium with twice its weight of violet potassium chromic chloride, $KCrCl_4$, or of a 1 : 2 mixture of potassium and chromic chlorides; and extracting the cold mass first with water, and then with dil. alkali-lye to remove free aluminium. G. Hindrichs found that mixtures with between 5 and 55 per cent. of chromium form two liquid layers, Fig. 10, and there is evidence of the formation of **aluminium trichromide,** $AlCr_3$, whose m.p. lies above 1600°. L. Guillet obtained alloys corresponding with *aluminium chromide,* AlCr, and *aluminium tetrachromide,* $AlCr_4$, in the form of silver-grey powders of the respective sp. gr. 4·93 and 6·75 at 20°. H. Schirmeister, J. W. Richards, and E. S. Sperry made some observations on these alloys. F. Wöhler regarded his product as the monochromide, and he described it as forming tin-white, tetragonal plates, or rectangular tetragonal prisms resembling idocrase. It melts at a higher temp. than nickel, forming, when cold, a hard, brittle mass of sp. gr. 4·9. When heated in air, it acquires a steel-coloured lustre without oxidizing further; when heated in hydrogen chloride, some silicon chloride is formed from the impurities present, chromous and aluminium chlorides are also produced; hydrochloric acid attacks the alloy with the evolution of hydrogen; warm, conc. sulphuric acid develops hydrogen with the separation of sulphur; and it is not attacked by conc. nitric acid, or alkali-lye.

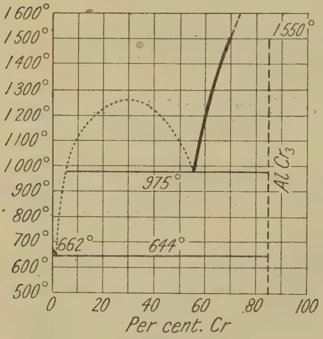


FIG. 10.—Freezing-point Curve of Al–Cr Alloys.

According to G. Hindrichs,[5] **tin-chromium alloys** are produced within a very narrow range; the f.p. of chromium is lowered by the addition of up to 10 per cent. of tin; and mixed crystals are formed up to 6 per cent. of tin—*vide* Fig. 11; beyond this, two liquid phases are formed one of which is pure tin. N. A. Puschin said that alloys are soft until about 90 at. per cent. Cr. is present, when they are hard and brittle; the e.m.f. curve of the cell Sn | *N*-KOH | SnCr_n shows no sign of either chemical combination or of solid soln. With *n* per cent. Cr, the potentials, *E* in millivolts, are:

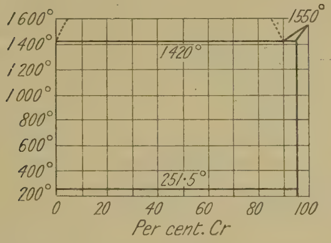


FIG. 11.—Freezing-point Curve of Sn–Cr Alloys.

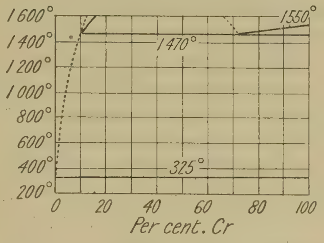


FIG. 12.—Freezing-point Curve of Pb–Cr Alloys.

n .	20	25	33	50	67	75	90	95·8	100
E .	−16	−2	−1	−1	−4	−3	−4	10	302

G. Hindrichs said that **lead-chromium alloys** can be formed by melting a mixture of the two elements above 1600°. Much lead is volatilized. The addition of 27 per cent. of lead lowers the f.p. of chromium 80°—*vide* Fig. 12; alloys with more than this proportion of lead separate into two layers one of which is lead alone, W. von Bolton obtained alloys with **tantalum and chromium.**

REFERENCES.

[1] G. Hindrichs, *Zeit. anorg. Chem.*, **59**. 420, 1908; E. Siedschlag, *ib.*, **131**. 173, 1923; R. Vogel and E. Trilling, *ib.*, **129**. 276, 1923; P. H. Hulin, *Brit. Pat. No.* 21543, 1902; E. Placet, *ib.*, 202, 203, 1896; Neo-Métallurgie Marbeau, *ib.*, 7847, 1895; Electrometallurgical Co., *German Pat., D.R.P.* 89348, 1896; L. P. Hamilton and E. F. Smith, *Journ. Amer. Chem. Soc.*, **23**. 151, 1901; D. S. Ashbrook, *ib.*, **26**. 1285, 1904; H. Goldschmidt, *Journ. Soc. Chem. Ind.*, **17**. 545, 1898; *Liebig's Ann.*, **301**. 25, 1898; L. Jordan, L. H. Grenall and H. K. Herschman, *Trans. Amer. Inst. Min. Met. Eng.—Min. Met.*, 1661, 1927; H. Moissan, *Compt. Rend.*, **119**. 185, 1894; **122**. 1302, 1896; A. B. du Jassonneix, *ib.*, **144**. 915, 1907; D. F. McFarland and O. E. Harder, *Bull. Eng. Univ. Illinois*, 93, 1912; M. G. Corson, *Brass World*, **22**. 289, 1926.

[2] H. le Chatelier, *Compt. Rend.*, **120**. 835, 1895; *Bull. Soc. Enc. Nat. Ind.*, (4), **10**. 388, 1895; G. Hindrichs, *Zeit. anorg. Chem.*, **39**. 427, 1908.

[3] T. Dieckmann and O. Hauf, *Zeit. anorg. Chem.*, **86**. 301, 1914; H. Moissan, *Ann. Chim. Phys.*, (5), **21**. 250, 1880; *Bull. Soc. Chim.*, (2), **31**. 149, 1879; *Compt. Rend.*, **88**. 180, 1879; J. Férée, *ib.*, **121**. 823, 1895; *Bull. Soc. Chim.*, (3), **25**. 619, 1901; G. Tammann and J. Hinnüber, *Zeit. anorg. Chem.*, **160**. 257, 1927; R. Myers, *Journ. Amer. Chem. Soc.*, **26**. 1126, 1904; C. F. Schönbein, *Pogg. Ann.*, **112**. 445, 1861; C. W. Vincent, *Phil. Mag.*, (4), **24**. 328, 1862; A. S. Russell, D. C. Evans, and S. W. Rowell, *Journ. Chem. Soc.*, **129**. 1881, 1926; A. S. Russell, *ib.*, 2398, 1929; M. Rabinovich and P. B. Zywotinsky, *Koll. Zeit.*, **52**. 31, 1930; N. Bunge, *Chem. Centr.*, (2), **10**. 257, 1865; Z. Roussin, *Chem. News*, **14**. 27, 1866; *Journ. Pharm. Chim.*, (5), **3**. 413, 1866; *Bull. Soc. Chim.*, (2), **6**. 23, 1866.

[4] J. W. Richards, *Journ. Franklin Inst.*, **157**. 394, 1904; C. Combes, *Compt. Rend.*, **122**. 1484, 1896; H. Moissan, *ib.*, **122**. 1302, 1896; *Le four électrique*, Paris, 1900; London, 1904; *Bull. Soc. Chim.*, (3), **15**. 1282, 1896; H. Schirmeister, *Stahl Eisen*, **35**. 649, 873, 896, 1915; *Beiträge zur Kenntnis der binären Aluminiumlegierungen hinsichtlich ihrer technischen Eigenschaften*, Düsseldorf, 1914; F. Wöhler, *Liebig's Ann.*, **106**. 118, 1858; L. Guillet, *Bull. Soc. Enc. Nat. Ind.*, **101**. ii, 252, 1902; *Gén. Civ.*, **41**. 363, 367, 393, 1902; G. Hindrichs, *Zeit. anorg. Chem.*, **59**. 414, 1908; E. S. Sperry, *Trans. Amer. Inst. Min. Eng.*, **29**. 280, 1029, 1899; F. T. Sisco and M. R. Whitmore, *Journ. Ind. Eng. Chem.*, **17**. 956, 1925.

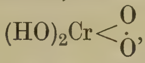
[5] G. Hindrichs, *Zeit. anorg. Chem.*, **59**. 414, 1908; N. A. Puschin, *Journ. Russ. Phys. Chem. Soc.*, **39**. 869, 1907; W. von Bolton, *Zeit. Elektrochem.*, **11**. 47, 1905.

§ 8. The Lower Chromium Oxides

The metals of the chromium family can produce an extraordinary number of compounds;[1] they can behave as 2-, 3-, 4-, 5-, 6-, and in some cases as 8-valent elements. Hence, one element can form nearly all the types of compounds which characterize the individual elements. The lower oxides have basic properties, while the higher oxides are markedly acidic; the intermediate oxides—like those of molybdenum, tungsten, and uranium dioxides—are indifferent oxides and resemble in some respects the peroxides of lead and manganese. The lowest oxide of chromium is a strong reducing agent, while the acidic oxide acts as a strong oxidizing agent. All these elements readily form oxides with a composition intermediate between two simpler oxides, and which appear to be salt-like compounds in which the higher oxide plays the rôle of acid, and the lower oxide, base. The intermediate oxides of chromium are not analogous with those of uranium—in the first case the intermediate oxide appears as a compound of the sesqui- and tri-oxides; and in the other case, a compound of the di- and tri-oxides. The existence of the dioxide of chromium is not so unequivocally established as the dioxides of molybdenum, tungsten, and uranium; and the peroxide behaves as if it were a compound of the tri- and sesqui-oxide. Three members of the group—molybdenum, tungsten, and uranium—are closely analogous in the nature of the oxides formed, but chromium differs in many ways from the others—*e.g.* in the unstability of chromic trioxide, and the formation of no chloride higher than $CrCl_3$.

A. Moberg[2] obtained **chromium monoxide,** or **chromous oxide,** CrO, by the action of hydrogen or the vapour of alcohol on red-hot chromic oxide, and by heating chromous chloride with sodium carbonate or calcium oxide. It was also similarly obtained by L. Clouet, and E. M. Péligot. J. Férée obtained the oxide by the decomposition of chromium-amalgam in air. T. Dieckmann and O. Hauf said that the oxide is most conveniently made by the action of dil. nitric acid on chromium amalgam; the mercury passes into soln., chromous oxide remains as a black powder. Hydrogen at 1000° reduces chromous oxide to the metal. According to J. Férée, when the black powder is triturated in a mortar, it oxidizes and glows, forming chromic oxide, and likewise also when heated in air. It is insoluble in dil. nitric or sulphuric acid, and it reacts with hydrochloric acid forming a blue soln., and giving off hydrogen. Carbon dioxide at 1000° converts it into a mixture of chromic oxide and carbide. The constancy of the analytical data by J. Férée favours the assumption that it is not a mixture of chromium and chromic oxide.

If air-free aq. soln. of chromous chloride be treated with an air-free soln. of potassium hydroxide, A. Moberg found that a yellow precipitate of **chromous hydroxide,** $Cr(OH)_2$, is formed. It should be washed with air-free water in an atm. of hydrogen, or carbon dioxide, and dried over sulphuric acid. It is then dark brown. It is stable in dry air, but decomposes when heated: $2Cr(OH)_2 = Cr_2O_3 + H_2O + H_2$; it dissolves slowly in conc. acids when freshly precipitated and dried; but very little dissolves in dil. acids; and very little in boiling aqua regia. The soln. are green, and contain tervalent chromium because, said A. Moberg, chromium separates as the hydroxide dissolves. F. Allison and E. J. Murphy studied the magneto-optic properties.

The salts of this base, **chromous salts,** are obtained by reducing chromic salts—*vide infra,* chromous sulphate or chloride. The aq. soln. are red, blue, or yellow. The chromous salts readily decompose in the presence of water, forming chromic salts and hydrogen; and hydrogen is evolved when the aq. soln. are boiled or treated with platinized platinum. R. Peters said that hydrogen is liberated in the oxidation because a chromous salt soln. has a higher potential than hydrogen when in acidic soln. The reaction was studied by R. Stahn. No hydrogen dioxide was observed by W. Manchot and J. Herzog to be formed during the oxidation of chromous salts by atm. oxygen; and the amount of oxygen absorbed is simply that required for the oxidation. Hence it is inferred that the oxidation proceeds directly. According to W. Manchot and O. Wilhelms, the primary oxide formed in the oxidation of these salts is a peroxide, say CrO_2, because in the presence of an acceptor—say alcohol, or potassium arsenite—which is simultaneously oxidized, two eq. of oxygen are absorbed for each eq. of chromous oxide. J. Piccard found that in the autoxidation of neutral or acidic soln. of chromous salts, chromic acid and chromic salts are formed. Intermediate products, stable for a measurable period, are formed—*vide infra*, chromous chloride. There is first, the easily decomposed hypothetical oxide, represented by $(HO)_2Cr.O.O.Cr(OH)_2$, which acts on potassium iodide in almost neutral soln. It decomposes into the labile oxide $CrO(OH)_2$ by a unimolecular reaction. This oxide in the absence of potassium iodide forms chromic acid, but in the presence of potassium iodide, it is reduced more rapidly than it can form chromic acid. The next oxide,  $(HO)_2Cr{<}\begin{matrix}O\\ \vert\\ O\end{matrix}$, is reduced by potassium iodide in weakly acidic soln. within two minutes. W. Traube and W. Lange found that with chromous hydroxide, oxalic, hydrocyanic, and thiocyanic acids are converted into glycollic acid, methylamine, and hydrogen sulphide, respectively. Azides and azoimide instantaneously yield nitrogen and ammonia. Chloroacetic acid is converted into acetic acid, whilst benzaldehyde yields benzyl alcohol—*vide infra*, chromous chloride.

R. Bunsen[3] reported an oxide $2CrO.Cr_2O_3$, or $3CrO.Cr_2O_3$, to be formed in the electrolysis of soln. of chromic salts—*vide supra*, the electrolytic preparation of chromium. The black, amorphous powder glows when heated in air forming green chromic oxide; it is insoluble in acids. A. Geuther could not prepare an oxide of this composition; and J. Férée obtained a black powder with similar properties, but with the composition $Cr_2O_3.H_2O$, in his study of the electrolysis of soln. of chromic chloride.

According to E. M. Péligot,[4] when an air-free aq. soln. of chromous chloride is treated with air-free alkali-lye in an inert atm., the brown precipitate which is formed gradually in the cold, rapidly when boiled, decomposes, hydrogen is evolved, and a reddish-brown hydrate of **chromosic oxide**, or **chromium tritatetraoxide**, Cr_3O_4, or $CrO.Cr_2O_3$, is formed. This can be washed with boiling water, and dried in vacuo. According to A. Moberg, and G. Baugé, it is a *trihydrate*, whereas E. M. Péligot said that it is a *monohydrate*. G. Baugé could not make the monohydrate, but he obtained the trihydrate, $Cr_3O_4.3H_2O$, by treating chromous carbonate with alkali carbonate in boiling water while protected from air. The brown powder loses water when heated, and it suffers autoxidation: $2Cr_3O_4+2H_2O=3Cr_2O_3+H_2+H_2O$. According to G. Baugé, when dried in vacuo at 100°, the yellowish-brown powder has a sp. gr. 3·49. It is converted into chromic oxide by the action at 250° of water-vapour, hydrogen chloride, or an inert gas, hydrogen being evolved; it is also decomposed by chlorine at a dull red-heat, giving chromyl chloride, water, and hydrogen chloride. Although stable in dry air at the ordinary temp., it is rapidly oxidized to chromic oxide in presence of water or when heated; by hydrogen sulphide, it is converted at a somewhat elevated temp. into a crystalline sulphide, whilst it rapidly reduces dil. sulphuric acid at 40°, hydrogen sulphide being evolved if a large quantity of the oxide is employed. When the latter is dissolved in conc. hydrochloric acid, a mixture of chromous and chromic chlorides is formed.

REFERENCES.

[1] W. Muthmann, *Liebig's Ann.*, **238**. 108, 1887.

[2] A. Moberg, *De oxydo chromoso*, Helsingfors, 1847; *Journ. prakt. Chem.*, (1), **43**. 119, 1843; T. Dieckmann and O. Hauf, *Zeit. anorg. Chem.*, **86**. 801, 1904; L. Clouet, *Compt. Rend.*, **67**. 762, 1868; E. M. Péligot, *Ann. Chim. Phys.*, (3), **12**. 528, 1864; *Compt. Rend.*, **67**. 871, 1868; J. Férée, *ib.*, **121**. 823, 1895; *Bull. Soc. Chim.*, (3), **25**. 619, 1901; W. Manchot and O. Wilhelms, *Liebig's Ann.*, **325**. 125, 1902; W. Manchot, *ib.*, **325**. 93, 1902; *Ueber Sauerstoff Activierung*, Würzburg, 1908; W. Manchot and J. Herzog, *Ber.*, **33**. 1742, 1900; R. Peters, *Zeit. phys. Chem.*, **26**. 216, 1898; J. Piccard, *Ber.*, **46**. 2477, 1913; W. Traube and W. Lange, *ib.*, **58**. B, 2773,

1925; R. Stahn, *Ein Beitrag zur Chemie des zweivertigen Chroms*, Berlin, 1926; F. Allison and E. J. Murphy, *Journ. Amer. Chem. Soc.*, **52**. 3796, 1930.

[3] R. Bunsen, *Pogg. Ann.*, **91**. 619, 1854; *Ann. Chim. Phys.*, (3), **41**. 354, 1854; A. Geuther, *Liebig's Ann.*, **118**. 66, 1861; J. Férée, *Bull. Soc. Chim.*, (3), **25**. 620, 1901.

[4] E. M. Péligot, *Ann. Chim. Phys.*, (3), **12**. 544, 1844; *Compt. Rend.*, **19**. 609, 734, 1844; **20**. 1187, 1845; **21**. 76, 1845; A. Moberg, *De oxydo chromoso*, Helsingfors, 1847; *Journ. prakt. Chem.*, (1), **43**. 119, 1843; G. Baugé, *Ann. Chim. Phys.*, (7), **19**. 178, 1900; *Compt. Rend.*, **127**. 551, 1898; *Sur quelques carbonates doubles du protoxyde de chrome*, Paris, 1899.

§ 9. Chromic Oxide

Chromium oxidizes when heated in air to form **chromium hemitrioxide, chromium sesquioxide,** or **chromic oxide,** Cr_2O_3; chromic oxide is also produced by calcining the hydroxide—*vide supra*, the extraction of chromium. The analysis of J. J. Berzelius [1] corresponds with this formula; and it is usually supposed to be constituted $O{=}Cr{-}O{-}Cr{=}O$; although A. T. Cameron assumed the formula to be $Cr{\equiv}O_3{\equiv}Cr$. L. N. Vauquelin, H. Moser, J. Persoz, and J. B. Trommsdorff obtained this oxide by heating mercuric chromate; it has a fine green colour if calcined out of contact with air, but it has a brown colour when heated while exposed to air. A. Maus obtained it by heating ammonium chromate; A. A. Hayes, ammonium dichromate: $(NH_4)_2Cr_2O_7{=}4H_2O{+}N_2{+}Cr_2O_3$; J. L. Lassaigne, and H. Moser, a mixture of potassium chromate and sulphur, and extracting the soluble products with water; G. C. Wittstein, H. C. Roth, and E. Dieterich, a mixture of potassium dichromate and sulphur; F. Wöhler, a mixture of potassium dichromate, ammonium chloride, and sodium carbonate; R. T. M. y Luna, G. B. Frankforter and co-workers, a mixture of potassium dichromate and ammonium chloride; and A. L. D. d'Arian, alkali chromate and ammonium sulphate. According to V. H. Roehrich and E. V. Manuel, the reaction between ammonium chloride and potassium dichromate, usually symbolized by R. T. M. y Luna's equation $2NH_4Cl{+}K_2Cr_2O_7{=}Cr_2O_3{+}2KCl{+}4H_2O{+}N_2$, varies with the temp. at which the mixture is heated and the relative proportions of the constituents of the mixture. The first visible sign of change occurs at 210° when the mixture becomes yellowish-brown owing to the formation of a chromium dioxide; at 260°, a slate-coloured residue is obtained which when lixiviated with water gives greenish-black crystals of a hydrated chromic oxide. At 370°, with an excess of ammonium chloride, chromium chloride and ammonia are formed; with the potassium dichromate in excess a black residue mixed with unchanged dichromate is formed. Under different conditions chlorine, nitric oxide, nitrogen peroxide and chromium nitride may be formed as by-products. C. H. Binder obtained chromic oxide by heating a mixture of potassium dichromate and starch; C. H. Humphries, from a mixture of chromium trioxide and barium hydroxide. R. Böttger inflamed a mixture of picric acid, potassium dichromate, and ammonium chloride; H. Schöffer inflamed a mixture of sodium dichromate and glycerol; W. Carpmael heated an aq. soln. of an alkali chromate and an organic reducing agent—sugar, sawdust, etc.—above 110°, under press.; and E. A. G. Street obtained it as a product in the electrolysis of a soln. of an alkali chromate with a mercury cathode. F. Wöhler, and J. F. Persoz found that the crystalline oxide is formed when chromyl chloride is decomposed by heat; W. P. Evans, when chromyl fluoride is heated; E. Frémy, when heated potassium chromate is decomposed by chlorine; W. Müller, when potassium chromate at a red-heat is decomposed by hydrogen chloride; V. Kletzinsky, when potassium chlorochromate is melted; J. C. Gentele, when potassium dichromate is decomposed at a high temp.; R. Otto, when potassium dichromate is decomposed by hydrogen at an elevated temp.; A. Ditte, and H. Schiff, when potassium dichromate is decomposed by fusion with sodium chloride; and M. Prud'homme, when potassium dichromate is heated with tin. Crystals of chromic oxide are often produced as a kind of sublimate when mixtures containing chromic oxide are heated in closed vessels in pottery ovens. E. Wydler, and G. F. C. Frick also described the preparation of the oxide; and W. P. Blake and W. H. Miller observed its formation as a furnace product. C. Ullgren obtained crystals of the oxide by decomposing potassium dichromate mixed with oil, or ammonium chloride and then raising the temp. to a white-heat. V. Kohlschutter and J. L. Tüscher obtained highly dispersed or an **aerosol of chromic oxide** by vaporizing the oxide into a chamber where it is suddenly chilled.

The physical properties of chromic oxide.—The **colour** of amorphous chromic oxide is bright green if it has been calcined in a reducing atm., and it may acquire a brown tinge in an oxidizing atm. The tint of commercial oxides varies from brownish-green, to greyish-green, to olive-green to bright grass-green. This may be due to partial crystallization; to the grain-size of the powder; and to the presence of traces of impurity as a result of which the colour of a chromate may be superposed on that of the chrome-green. The amorphous chromic oxide obtained from ammonium dichromate is a voluminous, tea-green powder. A very thin sublimate of chromic oxide is red, and this probably explains the colour of the chrome-tin pink, **1**. 46, 33; and of the ruby, **5**. 33, 10. R. Klemm found a relationship between the proportion of chromium in spinel, corundum, spodumene, beryl, chrysoberyl, topaz, and zircon and the depth of colour. In all but zircon, chromium replaces aluminium, and in zircon, it may replace silicon or zirconium. Small quantities of vanadium may take the place of chromium. Black chromic oxide, insoluble in acids, was obtained by L. Godefroy by heating the hydrate, $Cr_2O_3.3H_2O$; and by E. A. Werner, by heating the succinate. According to O. Hauser, the play of colours of the variety of chrysoberyl called *alexandrite* is produced by a small trace of chromic oxide. I have evidence that the colour of chrome-tin pink or crimson—produced by a trace of chromic oxide on stannic oxide as mordant—probably represents the colour of the highly dispersed chromic oxide. The colour can be produced by depositing the vapour of chromic oxide on stannic oxide or on alumina. According to A. Duboin and others, the colour of the ruby is due to the presence of chromic oxide—**5**. 33, 10. The red colour of the so-called chrome-tin crimson is thus equivalent to the crimson and purple colour of the purple of cassius where colloidal gold is dispersed on the same mordant; and also equivalent to the copper red—*rouge flambé*—where presumably colloidal copper is deposited on the same mordant. The chrome-tin crimson has been discussed by H. A. Seger, F. Rhead, A. S. Watts, R. C. Purdy and co-workers, W. A. Hull, W. A. Lethbridge, L. Petrik, and T. Leykauf—*vide infra*, stannic chromate. C. W. Stillwell said that the red colour of rubies is not due to colloidal chromic oxide; that it is not due to higher or lower oxides of chromium; nor to variations in the proportion of chromic oxide present. He assumed that the red colour is due to a second modification of chromic oxide, of the same crystal structure as the green modification and alpha alumina, whose axial ratio is nearer to that of alpha alumina than is the axial ratio of the green modification. Therefore, the red modification tends to form when chromic oxide is added to alpha alumina and does form under ordinary conditions up to a certain point, beyond which the effect of the alumina is not strong enough to stabilize it. The occurrence of the red or green modification depends on the value of the axial ratio of the mixed crystal. There is a discontinuity in the change of the axial ratio with change in chromic oxide content when one modification changes to the other. There is also a marked difference in the axial ratio of a mixed crystal containing the red form of chromic oxide and a crystal containing the same amount of chromic oxide in the green form. This change in axial ratio may be affected in two different ways—*e.g.* by varying the proportion of chromic oxide, or by varying the nature of the atm. in which the mixture is fused.

L. Blanc showed that the blue, amorphous oxide, which he designates α–Cr_2O_3, is rapidly transformed into the green, crystalline oxide—β–Cr_2O_3—at 700°. L. Blanc and G. Chaudron added that the exothermal passage of the blue, precipitated α–Cr_2O_3 to olive-green β–Cr_2O_3, occurs at 500° in air and at 750° in vacuo. The blue oxide absorbs oxygen rapidly at 200°, forming CrO_2 and Cr_5O_9. Both these form β–Cr_2O_3 and a black oxide at 440°, and if kept several hours at 350°, a larger proportion of the black oxide is formed. It is decomposed at 450°–500° yielding β–Cr_2O_3. Guignet's green, or finely divided β–Cr_2O_3, gives the black oxide on oxidation. Hence there are two oxides of the formula Cr_5O_9 with a transition temp. If the amorphous chromic oxide be heated in a gas-blowpipe, and cooled, E. Frémy, and M. Z. Jovitschitsch said that the product is crystalline ; and H. Moissan, also, by heating the oxide in the electric arc-furnace. T. Sidot crystallized the oxide by heating it in a current of oxygen ; J. J. Ebelmen, by strongly heating it with calcium carbonate and boric oxide ; and P. Ebell, by dissolving the oxide in molten glass at a high temp.—the oxide crystallizes out as the glass is slowly cooled.

Crystalline chromic oxide forms lustrous black **crystals,** or a green powder. According to G. Strüver, the trigonal crystals have the axial ratio $a : c = 1 : 1{\cdot}3770$, and $\alpha = 85° \ 22'$. The crystals were also examined by G. Rose, W. H. Miller, W. P. Blake, and J. J. Ebelmen. The **cleavage** on the (100)-face is well-defined. According to G. Rose, the crystals are isomorphous with the corresponding aluminium and ferric oxides. W. P. Davey found that the **X-radiograms** correspond with a diamond lattice except that the cube is stretched along its body-diagonal. The side of the unit triangle is 4·745 A. ; and the high axial ratio, 2·764, is explained by assuming a hexahedral molecule consisting of an equilateral triangle of oxygen with a metal atom immediately above and below the centre of the triangle ; there are three molecules per unit prism—**5.** 33, 10. W. H. Zachariasen made observations on this subject and obtained for the axial ratio $a : c = 1 : 1{\cdot}374$; and for the parameter $r = 5{\cdot}35$ A. L. Passerini gave for the hexagonal cell $a = 4{\cdot}950$ A., $c = 6{\cdot}806$ A. ; with $a : c = 1 : 1{\cdot}374$, $v = 143{\cdot}4 \times 10^{-24}$ c.c., and density 5·283 ; and for the rhombohedral cell, $a = 5{\cdot}38$ A., and $\alpha = 54° \ 50'$; whilst P. E. Wretblad gave for the hexagonal cell, $a = 4{\cdot}949$ A., $c = 13{\cdot}57$ A., $a : c = 1 : 2{\cdot}7412$, and $\alpha = 55° \ 11'$. L. Passerini, and V. M. Goldschmidt and co-workers studied the solid soln. with alumina, and with ferric oxide (*q.v.*). W. Müller said that the oxide prepared by reducing potassium chromate with dry—not moist—hydrogen chloride is quite different from the ordinary oxide, being greyish-green, composed of tube-like plates of the hardness of graphite.

F. Wöhler found the **specific gravity** of the crystalline oxide to be 5·21 ; L. Playfair and J. P. Joule gave 4·909 ; H. Schröder, 5·010 ; H. Schiff, 6·2 ; W. A. Roth and G. Becker, 5·20 to 5·21 at 21° ; and E. Wedekind and C. Horst, 5·21 ; L. Blanc found that the oxide calcined from 500° to 800° has a sp. gr. 5·033 ; at 820°, 5·110 ; at 1080°, 5·130 ; and when fused, 6·145. H. P. Walmsley gave 5·238 for the sp. gr. of the dispersed oxide ; and W. H. Zachariasen, 5·25, calculated from the X-radiogram data. W. Biltz and co-workers found the mol. vol. of chromic oxide in the spinels to be 28·9. F. Wöhler found that crystalline chromic oxide has a **hardness** great enough for it to scratch quartz, topaz, and hyacinth ; and G. Rose, and W. P. Blake found that it is as hard as corundum. O. Ruff and A. Riebeth discussed the **plasticity** of mixtures of the oxide with water, etc.

H. V. Regnault gave 0·1796 for the **specific heat ;** F. E. Neumann, 0·196 ; and H. Kopp, 0·177 for the crystalline oxide. A. S. Russell found 0·0711 for the sp. ht. between −191° and −80·3° ; 0·1474, between −76·5° and 0° ; and 0·1805, between 2·6° and 49·3° and for the **molecular heat,** 10·81 at −136° ; 22·40 at −38° ; and 27·4 at 26°. J. Maydel discussed some relations of the sp. ht. J. J. Berzelius, H. Moissan, and J. Weise observed that the precipitated hydrated oxide exhibits **calorescence** when heated—*vide* alumina, **5.** 33, 10—and at the same time becomes denser, and less soluble in acids. W. G. Mixter said that the glowing occurs between 500° and 610°. J. J. Berzelius, L. Wöhler, and K. Endell and R. Rieke gave 500° ; H. le Chatelier, 900° ; L. Blanc, 550° to 600° ; G. Rothaug, 420° to 680°, according as the precipitate is pulverulent or granular—and he added that particles may be projected from the crucible at this temp. H. Moissan, H. le Chatelier, and W. G. Mixter regarded the change as evidence of the passage from one allotropic form to another. L. Wöhler found that the calorescence is independent of the surrounding atm. and the humidity. The temp. of calorescence is lowered by increasing the quanity of material. With 8 grms. of chromic oxide, the temp. in dry hydrogen is 530°–550°, although in air or oxygen it begins at 425° on account of the exothermal decomposition of the chromium dioxide which is formed. The calorescence is hindered by precipitation with ammonia from soln. containing sulphate, and favoured by a low conc. of the chromic salt soln. L. Wöhler and M. Rabinowitsch found that the thermal value of the calorescence is 8 to 11 cals. per gram according as the oxide is precipitated from conc. or dil. soln. The change to the sintered oxide by calorescence is never complete. The oxide formed with the greatest heat development is the best absorbent for *m*-nitrobenzoic acid. M. Siewert showed that the glowing temp. depends on the rate of heating; and L. Wöhler, that the glowing is increased by conditions which favour hydrosol formation in the preparation of the hydrated oxide; and it is greater in proportion to the adsorption capacity of the precipitate. This agrees with the hypothesis that the phenomenon is connected with the surface area of the particles, and is due to a sudden decrease in the large surface of the oxide prepared by precipitation. J. Böhm found that the X-radiograms of chromic oxide before and after the calorescence showed that the glowing is attended by the passage of the oxide from the amorphous to the crystalline state. E. D. Clark found that chromic oxide melts in the oxy-hydrogen blowpipe flame giving off white fumes, but without reduction; E. Tiede and E. Birnbräuer studied the action of high temp. on the oxide. H. Moissan melted it in the electric furnace. C. W. Kanolt gave 1990° for the **melting point** of chromic oxide. L. Elsner observed that chromic oxide volatilizes in the porcelain ovens—presumably at 1500°–1600°. I have noticed evidence of its volatilization in pottery ovens at as low a temp. as 1050°; and C. Zengelis obtained evidence of its volatilization at ordinary temp. W. R. Mott gave 3000° as an approximation to the **boiling point.** F. Born calculated the **dissociation pressure** of chromic oxide at 2000° to be 3 mm., and at 3000°, over 760 mm. H. von Wartenberg and S. Aoyama gave for the partial press. of the oxygen at 600° and 1130° respectively $p_{O_2}=6{\cdot}73\times10^{-37}$ and $3{\cdot}07\times10^{-13}$. W. G. Mixter gave for the **heat of formation** of crystalline chromic oxide $(2Cr,1\frac{1}{2}O_2)$ $=267{\cdot}8$ Cals.; for the stable amorphous oxide, 266 Cals.; and for the unstable oxide, 243 Cals. H. von Wartenberg gave 265·8 Cals.; and W. A. Roth and G. Becker, 288·0 Cals. H. von Wartenberg and S. Aoyama calculated 279 Cals. The subject was discussed by H. Collins.

E. L. Nichols and B. W. Snow measured the **reflecting power** of chromic oxide; and M. Luckiesh found that for light of wave-length λ in μ:

λ . .	0·44	0·48	0·54	0·56	0·60	0·64	0·70
Light green .	10	14	23	20	11	9	6 per cent.
Medium green	7	10	17	13	7	6	5 per cent.

W. W. Coblentz found for the ultra-red reflecting power:

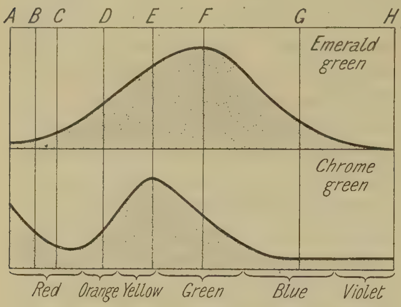
λ	0·60	0·95	4·4	8·8	24·0μ
Reflecting power .	27	45	33	5	8 per cent.

and for the **ultra-red emission spectrum,** he obtained for the diffuse reflecting power:

λ	0·54μ	0·60μ	0·95μ	4·4μ	8·8μ	24·0μ
Emission . .	24·1	27·0	46·4	32·9	5·0	8·2

The results are illustrated by Fig. 15, where the green oxide furnishes a fairly smooth spectrum with a possible maximum at 5μ, and a depression at 3·2μ. H. Schmidt-Reps studied this subject. G. Liebmann found the emissive power for visible red-light between 1208° K. and 2000° K. decreases with decreasing grain-size; it is independent of temp.; and increases rapidly with decreasing wave-length—*e.g.* for green light.

A. Dufour examined the **flame spectrum**; K. Skaupy, the heat radiation from the incandescent oxide; and W. N. Hartley, the spectrum of the oxide in the oxy-hydrogen flame. G. H. Hurst showed that with emerald-green pigment nearly all the green rays are reflected and only a small proportion of other rays, Fig. 13, while with chrome-green pigment, the green rays are reflected nearly in their full intensity, Fig. 14, but there is also reflected a portion of the red, blue, and violet rays. Hence the deeper tone of chrome-green in comparison with emerald-green. T. Dreisch studied the ultra-red absorption spectrum of glass coloured with chrome oxide. R. Robl observed but a faint luminescence in ultra-violet light. H. S. Patterson and R. Whytlaw-Gray studied the photophoresis of chromic oxide aerosols; and R. Whytlaw-Gray and co-workers, and E. Thomson found that particles exhibiting the Brownian movement form chains in an electrostatic field. C. Doelter observed no coagulation in radium rays; W. P. Jorrissen and H. W. Woudstra also studied the phenomenon. J. Vrede found the oxide to be of no use as a **radio-detector**.



FIGS. 13 and 14.—Reflection Spectra of Emerald-green and Chrome-green.

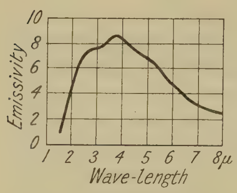


FIG. 15. — Ultra-red Emission Spectrum of Chromic Oxide.

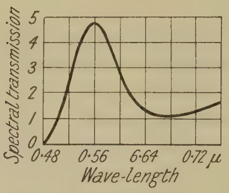


FIG. 16.—Spectral Transmission Factor of Chrome Green.

E. Friederich calculated $2\cdot9\times10^9$ for the **electrical resistance** of a metre of wire 1 sq. mm. section. According to M. Faraday, and L. F. Nilson and O. Pettersson, chromic oxide is magnetic. S. Meyer found the **magnetic susceptibility** to be $X=24\times10^{-5}$ mass units at 17°; and E. Moles and F. Gonzalez, $26\cdot2\times10^{-6}$. Comparative measurements were made by P. Hausknecht. E. Wedekind and co-workers gave $25\cdot97\times10^{-1}$ mass units at 16°; L. Blanc and G. Chaudron found an abrupt increase at 880° followed by a fall at 900°. G. Chaudron and H. Forestier observed that the coeff. of susceptibility of calcined chromic oxide is greater than that of the uncalcined oxide. S. Veil studied this subject. K. Honda and T. Sone gave :

	−186°	−64°	−3°	17·6°	64°	117°	644°	1335°
$\chi\times10^6$ . .	20·1	22·2	24·6	25·5	26·0	25·6	17·7	12·6

The chemical properties of chromic oxide.—E. D. Clarke said that chromic oxide is not decomposed by the oxyhydrogen blowpipe flame; and J. J. Berzelius found that it is not decomposed by **hydrogen** at a red-heat. For the electroxidation of chromic oxide, *vide* chromic acid, etc. According to R. Saxon traces of chromic acid are formed by the anodic oxidation of chromic oxide in pure water; the addition of manganese dioxide to the chromic oxide increases slightly the yield of chromic acid. Much more rapid oxidation ensues in the presence of calcium or potassium hydroxide or both. In soln. of alkali chlorides containing a little chrome-alum, chromic oxide is rapidly oxidized at the anode to chromic acid. K. Fischbeck and E. Einecke found that powdered chromic oxide is not perceptibly reduced when used as anode in the electrolysis of 2 per cent. sulphuric acid. The adsorption of hydrogen by the $ZnO–Cr_2O_3$ catalyst was studied by W. E. Garner and F. E. T. Kingman; whilst O. Schmidt, and A. F. Benton studied the adsorption of hydrogen by chromic oxide; and also the adsorption of **oxygen**. H. N. Warren, and H. von Wartenberg found that chromic oxide is reduced to the metal by hydrogen at 5 atm. press., and at 2500° ; and E. Newbery and J. N. Pring, by hydrogen at 2000° and 150 atm. press. H. von Wartenberg and S. Aoyama found that whereas iron oxides are reduced at 1100° when pH_2O/pH_2 is about 1, this ratio must be about 0·001 for the reduction of chromic oxide. Hence, since water is produced in the reduction, an enormous excess of hydrogen would be needed to reduce any quantity of chromic oxide, and there is no possibility of such a process being used instead of the alumino-thermic process for preparing carbon-free chromium. The heat of reaction calculated from these results agrees with the value for the heat of formation of chromic oxide from chromium, and it is inferred that chromous oxide is not an intermediate stage at these temp. (600–1400°)—*vide supra*, chromium. H. Moissan found that when chromic oxide is heated in oxygen to about 440°, some chromium dioxide is formed which decomposes into ordinary chromic oxide at a higher temp. According to L. and P. Wöhler, no oxidation occurs when chromic oxide is heated to 1220°, and they suggest that the formation of higher oxides must be an endothermal process taking place at higher temp. If chromic oxide is heated along with potassium sulphate in an atm. of oxygen at about 1000°, an equilibrium press. is established, which increases when the temp. is lowered, and decreases when the temp. is raised. This is therefore a case of exothermic dissociation, and the equilibrium is probably : $2K_2SO_4+Cr_2O_3+3O\rightleftharpoons 2K_2SO_4+2CrO_3$. The value of the equilibrium press. at any temp. varies with the quantity of oxygen already absorbed, probably because at 1000° potassium sulphate is fused and keeps the complex compound in soln. G. Rothaug found that the formation of chromic chromate, $5Cr_2O_3+9O\rightleftharpoons 2Cr_2(CrO_4)_3$, is a maximum at 300° and can be observed at 100°. The rate of the oxidation falls rapidly to 400°, and after that proceeds slowly. R. Schwarz added that the ignition of chromic oxide is best carried out in a platinum crucible since the reducing gases passing through the platinum hinder the formation of the chromic chromate, Cr_5O_{12}. Chromic oxide is insoluble in **water**—for the hydrates, *vide infra*. The oxide which has not been heated above the temp. at which it caloresces is more chemically active than otherwise. Thus, M. Traube and others showed that the chromic oxide obtained at a low temp. dissolves slowly, if at all, in **acids,** but not so if the oxide has been heated to a high temp. H. le Chatelier gave 900° as the temp. at which chromic oxide becomes insoluble in acids. A. Mailfert observed that **ozone** oxidizes chromic oxide. H. Moissan found that at 400°, moist **chlorine** reacts with dry chromic oxide forming chromyl chloride ; and R. Weber found that if the oxide has been dehydrated below the temp. of calorescence, it is easily attacked by dry chlorine to form chromyl chloride ; the calcined oxide is attacked by chlorine at a red-heat. If the chromic oxide is mixed with carbon, and heated in a current of dry chlorine, chromic chloride is formed. H. Moissan observed that the calcined oxide is not attacked by chlorine or by **bromine ;** and J. Weise added that the calcined oxide can be dissolved by **hydrofluoric acid** if a trace of chromic anhydride is present. K. Fredenhagen and G. Cadenbach found chromic oxide to be indifferent towards hydrofluoric acid. The attack by chlorine was studied by R. Wasmuth. O. Ruff and H. Krug found that chromic oxide is attacked with incandescence by **chlorine trifluoride**. G. Gore observed that liquid **hydrogen chloride** does not dissolve any chromic acid during 6 days' digestion.

J. L. Lassaigne, and K. Brückner found that chromic oxide is not attacked by **sulphur** vapour at a white-heat. H. Moissan observed that the oxide which has not been heated to a high temp. forms chromic sulphide when heated to 440° in a current of **hydrogen sulphide ;** but the calcined oxide is not attacked by this gas. C. Matignon and F. Bourion observed that when the oxide is heated in a current of **sulphur monochloride** and chlorine, chromic chloride is formed ; and R. D. Hall obtained a similar product with sulphur monochloride alone. F. Bourion found that the reaction begins at about 400°. G. Darzens and F. Bourion found that **thionyl chloride** at 400° also converts the chromic oxide into the chloride. L. and

P. Wöhler observed that **sulphur dioxide** does not reduce the oxide at a red-heat; and L. and P. Wöhler and W. Plüddemann studied its catalytic action in the oxidation of sulphur dioxide. H. P. Cady and R. Taft found the oxide to be insoluble in liquid sulphur dioxide, while chromic oxide which has been calcined at a high temp. does not dissolve in **sulphuric acid.** J. Weise said that if a trace of chromic acid be present, chromic oxide passes into soln. T. Sabalitschka and F. Bull said that fusion with **sodium pyrosulphate** is the best way to bring ignited chromic oxide into soln.

H. C. Wolterick found that when a mixture of **nitrogen** and hydrogen is passed over chromic oxide at 550°, a little ammonia is formed, and, according to H. N. Warren, some nitride as well; O. Schmidt studied the adsorption of nitrogen by chromic oxide, and also of **ammonia**. J. E. Ashby found that heated chromic oxide favours the combustion of ammonia in air. D. Maneghini studied it as a catalyst in the oxidation of ammonia. F. Ephraim observed that chromic oxide is attacked by **sodium amide**. M. Z. Jovitschitsch found that chromic oxide dissolves when digested for 10 hrs. with fuming or conc. **nitric acid;** the calcined oxide does not dissolve in nitric acid. R. Weber found that if strongly heated with **phosphorus pentachloride** chromic oxide furnishes the chloride. C. Lefèvre studied the action of **alkali arsenates** on chromic oxide.

J. J. Berzelius found that chromic oxide at a white-heat is decomposed by **carbon;** and H. C. Greenwood added that the reaction begins at about 1180°—*vide supra*, chromium. R. E. Slade and G. I. Higson said that the equilibrium press. of the oxide in contact with carbon at 1292° is 6·2 mm., and at 1339°, 9·2 mm. O. Heusler found that the carbon monoxide press. between 1480° and 1801° increases from 18 to 760 mm. The energy consumption for the liberation of a mol of carbon-monoxide is 52·8 Cals. The equilibrium between 886° and 1096° is represented by $\log K=11{\cdot}375-11550p^{-1}$. J. F. Gmelin, F. Göbel, and I. L. Bell observed that chromic oxide is not reduced by **carbon monoxide,** and G. Charpy said that this gas does not act on chromic oxide at 1000°. K. Chakravarty and J. G. Ghosh studied its catalytic action on the reaction between carbon monoxide and hydrogen; and W. E. Garner and F. E. T. Kingman, the adsorption of the gas by the $ZnO-Cr_2O_3$ catalyst. O. Schmidt, and A. F. Benton studied the adsorption of carbon monoxide and of **carbon dioxide** by chromic oxide; and O. Schmidt of **ethane** and **ethylene.** E. Demarçay, and H. Quantin found that **carbon tetrachloride** reacts with chromic oxide at a red-heat forming chromic chloride, phosgene, and carbon dioxide. P. Camboulives said that the reaction occurs at 580°. H. Rose observed that **carbon disulphide** at a white-heat forms chromic sulphide (*q.v.*). A. Kutzelnigg observed no oxidizing action on a soln. of **potassium ferrocyanide**. J. Milbauer found that molten **potassium thiocyanate** forms the sulpho-salt $K_2Cr_2S_4$. J. E. Ashby, J. R. Huffmann and B. F. Dodge, W. E. Garner and F. E. T. Kingman, W. A. Lazier, and H. H. Storch observed the catalytic action of chromic oxide in the oxidation of **alcohol, ether,** and **volatile oils**. W. Eidmann found chromic oxide to be insoluble in **acetone;** and H. Bodenbender found it to be soluble in a soln. of **calcium sucrate**—a litre of a soln. containing 418·6 grms. of sugar and 34·3 grms. of calcium oxide dissolves 1·07 grms. Cr_2O_3; a litre of a soln. containing 296·5 grms. of sugar and 24·2 grms. of calcium oxide dissolves 0·56 grm. of Cr_2O_3; and a litre of a soln. with 174·4 grms. of sugar and 14·1 grms. of calcium oxide dissolves 0·20 grm. of Cr_2O_3. A. Löwenthal studied its catalytic action in the oxidation of hydrocarbons and alcohol; L. J. Simon, the oxidation of organic substances; M. R. Fenske and P. K. Frolich, the formation of alcohol from carbon monoxide and hydrogen; J. R. Hoffman and B. F. Dodge, the formation and decomposition of methanol; and A. E. Tschitschibabin, the reaction between ammonia and acetylene. The use of chromic oxide as a mordant in the dyeing of **wool, cotton,** and **silk** was discussed by L. Liechti and J. J. Hummel, and W. D. Bancroft. The last-named said that from dichromate soln. wool first adsorbs chromic acid and this is reduced to chromic oxide, which is the true mordant; within limits, increasing the acid conc. increases the chromic acid taken up ; chromic acid oxidizes organic compounds more readily in presence than in absence of wool ; when wool is mordanted with chrome alum, a basic sulphate changing later to chromic oxide is first formed ; silk adsorbs chromic oxide less strongly than wool does ; cotton takes up scarcely any chromic oxide from chrome alum, but adsorbs it from an alkali soln. ; there is no evidence of the formation of any definite compound when wool is mordanted with chromic oxide. A. W. Davison discussed the adsorption of chromic oxide by **leather ;** H. Rheinboldt and E. Wedekind, the adsorption of organic dyes by chromic oxide.

A. Fodor and A. Reifenberg found that **silicic acid** peptizes ignited chromic oxide forming a colloidal soln. W. Guertler showed that the oxide is slightly soluble in molten **boric oxide** producing a green coloration. S. Kondo, and C. E. Ramsden examined the solubility of chromic oxide in pottery **glazes.** The reducing action of **boron** on heated chromic oxide was observed by A. Binet du Jassonneix ; of **silicon,** by B. Neumann, and P. Askenasy and C. Ponnaz. L. Kahlenberg and W. J. Trautmann observed that when mixed with silicon, there is no reaction if heated by a bunsen burner, a slight reaction at a cherry-red heat, and a good reaction in the electric arc. E. N. Bunting studied the binary system of chromic oxide and **silica.** H. von Wartenberg and H. Werth found that when heated with **zirconia,** no compound is formed, but a eutectic appears at about 2200° with about 50 per cent. of chromic oxide.

The reducing action of **potassium** and **sodium** was observed by J. J. Berzelius ; of **calcium,** by A. Burger ; of **magnesium,** by J. Parkinson, and L. Gattermann—*vide supra*, chromium ; of **aluminium**—*vide supra*, chromium ; and the colouring effect on glass by K. Fuwa. For the action of **metal oxides,** *vide infra*, the chromites. H. D. Rankin got chromite into soln. by heating it to redness and afterwards treating it with alkali-lye under press. H. Schiff found that chromic oxide is attacked with difficulty by fused **potassium nitrate.** According to J. von Liebig and F. Wöhler, E. Bohlig, and F. H. Storer, chromic oxide is attacked and oxidized by fused **potassium chlorate, hydrosulphate,** and **permanganate ;** by any suitable base in the presence of air or oxygen ; and by **lead dioxide,** or **manganese dioxide** in the presence of sulphuric acid. For the action of permanganates, *vide* the permanganates. T. Sabalitschka and F. Bull said that chromic oxide is incompletely soluble in fused **potassium pyrosulphate ;** to open the oxide up for analysis, it is preferable to fuse the substance with a mixture of 2 parts of sodium carbonate and 1 part of potassium nitrate for 10 min. The mass is dissolved in water and the insoluble residue fused with pyrosulphate. F. Hans found that chromic salts are oxidized by silver salts in accord with $Cr_2O_3+3Ag_2O=2CrO_3+6Ag$. J. Hargreaves and T. Robinson found that when mixed with **alkali chloride,** and heated in air or oxygen, chlorine is evolved, and in moist air, hydrogen chloride.

References.

[1] L. N. Vauquelin, *Journ. Phys.*, **45**. 393, 1794 ; **46**. 152, 311, 1798 ; *Journ. Mines.*, **6**. 737, 1797 ; *Nicholson's Journ.*, **2**. 387, 441, 1799 ; *Phil. Mag.*, **1**. 279, 361, 1798 ; **2**. 74, 1798 ; *Ann. Chim. Phys.*, (1), **25**. 21, 194, 1798 ; (1), **70**. 70, 1809 ; H. Moser, *Chemische Abhandlung über das Chrom*, Wien, 1824 ; *Schweigger's Journ.*, **42**. 99, 1824 ; J. F. Gmelin, *Comment. Gött.*, **14**. 20, 1799 ; J. B. Trommsdorff, *Trommsdorff's Journ.*, **2**. 366, 1795 ; A. A. Hayes, *Amer. Journ. Science*, (1), **14**. 136, 1828 ; (1), **20**. 409, 1831 ; W. P. Blake, *ib.*, (2), **10**. 352, 1850 ; W. G. Mixter, *ib.*, (4), **26**. 125, 1908 ; (4), **39**. 295, 1915 ; A. Maus, *Pogg. Ann.*, **9**. 127, 1827 ; **11**. 83, 1827 ; F. Wöhler, *ib.*, **10**. 46, 1827 ; **33**. 341, 1834 ; J. von Liebig and F. Wöhler, *ib.*, **24**. 171, 1832 ; W. Müller, *ib.*, **127**. 404, 1866 ; H. Schröder, *ib.*, **106**. 226, 1859 ; H. Rose, *ib.*, **42**. 541, 1837 ; G. Rose, *ib.*, **33**. 344, 1834 ; R. Weber, *ib.*, **107**. 375, 1859 ; **112**. 619, 1861 ; G. F. C. Frick, *ib.*, **13**. 494, 1828 ; F. E. Neumann, *ib.*, **23**. 1, 1831 ; J. L. Lassaigne, *Ann. Chim. Phys.*, (2), **14**. 299, 1820 ; R. T. M. y Luna, *ib.*, (3), **68**. 183, 1863 ; J. J. Ebelmen, *ib.*, (3), **22**. 211, 1847 ; H. V. Regnault, *ib.*, (3), **1**. 129, 1841 ; P. Sabatier and A. Mailhe, *ib.*, (8), **20**. 289, 1910 ; G. C. Wittstein, *Repert. Pharm.*, **66**. 65, 1839 ; A. F. Duflos, *Brandes' Arch.*, **23**. 166, 1827 ; E. Dieterich, *Bayer. Kunst. Gewerbebl.*, 549, 1866 ; *Zeit. Chem.*, (2), **2**. 273, 1866 ; C. H. Binder, *Rev. Science Ind.*, (2), **4**. 425, 1845 ; *Liebig's Ann.*, **60**. 203, 1846 ; H. Schiff, *ib.*, **106**. 114,

1858; **118**. 30, 1858; R. Otto, *ib.*, **142**. 102, 1866; M. Traube, *ib.*, **66**. 88, 1848; R. Böttger, *ib.*, **47**. 339, 1843; H. Schöffer, *Journ. Pharm. Chim.*, (5), **27**. 522, 1893; E. Frémy, *Ann. Chim. Phys.*, (3), **12**. 458, 1844; *Compt. Rend.*, **44**. 634, 1857; C. Lefèvre, *ib.*, **111**. 36, 1890; T. Sidot, *ib.*, **69**. 201, 1869; H. Moissan, *Ann. Chim. Phys.*, (5), **21**. 243, 1880; *Bull. Soc. Chim.*, (2), **34**. 70, 1880; *Compt. Rend.*, **90**. 82, 359, 1880; **115**. 1035, 1892; A. Ditte, *ib.*, **134**. 336, 1902; C. Matignon and F. Bourion, *ib.*, **138**. 760, 1904; F. Bourion, *Ann. Chim. Phys.*, (8), **21**. 56, 1901; G. Darzens and F. Bourion, *Compt. Rend.*, **133**. 271, 1911; E. Demarçay, *ib.*, **104**. 112, 1887; H. C. Wolterick, *ib.*, **146**. 124, 1908; H. Quantin, *ib.*, **104**. 223, 1887; A. Dufour, *ib.*, **148**. 1594, 1909; P. Camboulives, *ib.*, **150**. 175, 1910; G. Charpy, *ib.*, **148**. 560, 1909; A. Binet du Jassonneix, *ib.*, **143**. 897, 1906; **144**. 915, 1907; J. Persoz, *ib.*, **53**. 69, 1861; A. Mailfert, *ib.*, **94**. 797, 860, 1186, 1882; L. Blanc and G. Chaudron, *ib.*, **180**. 289, 1925; E. D. Clarke, *The Gas Blowpipe*, London, 1819; W. R. Mott, *Trans. Amer. Electrochem. Soc.*, **39**. 255, 1918; C. W. Stillwell, *Journ. Phys. Chem.*, **30**. 1441, 1926; L. Petrik, *Tonind. Ztg.*, **15**. 101, 1891; A. S. Watts, *Trans. Amer. Cer. Soc.*, **13**. 301, 1911; F. Rhead, *ib.*, **13**. 324, 1911; R. C. Purdy and G. H. Brown, *ib.*, **11**. 228, 1909; R. C. Purdy and A. S. Rea, *ib.*, **12**. 518, 1911; R. C. Purdy, *ib.*, **5**. 249, 1903; **14**. 178, 1912; W. A. Hull, *ib.*, **4**. 230, 1902; H. A. Seger, *Gesammelte Schriften*, Berlin, 541, 1908; Easton, Pa., **2**. 663, 1902; W. A. Lethbridge, *Trans. Cer. Soc.*, **3**. 9, 1903; T. Leykauf, *Journ. prakt. Chem.*, (1), **19**. 127, 1840; (2), **19**. 127, 1892; S. Kondo, *Bull. Tokyo Tech. School.*, 3, 1925; E. Wedekind and C. Horst, *Ber.*, **48**. 105, 1915; E. Wedekind and W. Albrecht, *ib.*, **59**. B, 1726, 1926; K. Honda and T. Sone, *Science Rep. Tohoku Univ.*, **3**. 223, 1914; C. W. Kanolt, *Journ. Washington Acad.*, **3**. 315, 1913; W. W. Coblentz, *Investigations of Infra-red Spectra*, Washington, **7**. 119, 1908; *Bull. Bur Standards*, **9**. 283, 1912; *Journ. Franklin Inst.*, **174**. 548, 1912; M. Luckiesh, *ib.*, **184**. 73, 227, 1917; S. Meyer, *Wied. Ann.*, **68**. 325, 1899; **69**. 236, 1899; *Ann. Physik*, (4), **1**. 664, 1900; C. Ullgren, *Berzelius' Aersberättelse Fys. Kemi.* 144, 1835; C. E. Ramsden, *Trans. Cer. Soc.*, **7**. 21, 1910; E. Bohlig, *Zeit. anal. Chem.*, **9**. 357, 1890; F. H. Storer, *Proc. Amer. Acad.*, **4**. 338, 1860; *Chem. News.*, **1**. 253, 265, 301, 1860; H. von Wartenberg and S. Aoyama, *Zeit. Elektrochem.*, **33**. 144, 1927; H. von Wartenberg, *Zeit. anorg. Chem.*, **151**. 326, 1926; O. Heusler, *ib.*, **154**. 353, 1926; F. Hans, *ib.*, **140**. 337, 1924; K. Fischbeck and E. Einecke, *ib.*, **167**. 21, 1927; L. Kahlenberg and W. J. Trautmann, *Trans. Amer. Electrochem. Soc.*, **39**. 377, 1921; G. N. Pearce and A. M. Alvarado, *Journ. Phys. Chem.*, **29**. 257, 1925; V. M. Goldschmidt, T. Barth and G. Lunde, *Skrift. Norske Akad.*, 7, 1925; P. Ebell, *Dingler's Journ.*, **220**. 64, 1876; M. Prud'homme, *Bull. Soc. Mulhouse*, **39**. 599, 1889; W. P. Evans, *Zeit. angew. Chem.*, **4**. 18, 1891; O. Hauser, *ib.*, **23**. 1464, 1910; W. H. Miller, *Phil. Mag.*, (4), **16**. 293, 1858; J. E. Ashby, *ib.*, (4), **6**. 77, 1853; G. Gore, *ib.*, (4), **29**. 541, 1865; E. L. Nichols and B. W. Snow, *ib.*, (5), **32**. 401, 1897; V. Kletzinsky, *Zeit. Chem.*, (2), **2**. 127, 1866; *Mitteilung aus dem Gebiete der reinen und angewandten Chemie*, Wien, 1865; J. C. Gentele, *Oefvers. Akad. Förh.*, 4, 1851; *Journ. prakt. Chem.*, (1), **81**. 418, 1860; J. F. Persoz, *L'Inst.*, **2**. 51, 143, 1834; G. Strüver, *Zeit. Kryst.*, **19**. 207, 1891; *Mem. Accad Lincei*, (4), **5**. 519, 1889; E. A. G. Street, *Brit. Pat. No.* 11879, 1899; O. Ruff and A. Riebeth, *Zeit. anorg. Chem.*, **173**. 373, 1928; A. Riebeth, *Plastische Masse mit verschiedenen anorganischen Stoffen und die Möglichkeiten ihrer keramischen Verwertung*, Breslau, 1927; W. H. Zachariasen, *Skrift. Norske Akad.*, 4, 1928; H. P. Walmsley, *Phil. Mag.*, (7), **7**. 1097, 1929; W. P. Jorrissen and H. W. Woudstra, *Koll. Zeit.*, **8**. 8, 1911; **10**. 280, 1912; C. Doelter, *Das Radium und die Farben*, Dresden, 1910; M. R. Fenske and P. K. Frolich, *Journ. Ind. Eng. Chem.*, **21**. 1052, 1929; J. R. Hoffman and B. F. Dodge, *ib.*, **21**. 1056, 1929; H. C. Roth, *U.S. Pat. No.* 1728510, 1929; J. Weise, *German Pat., D.R.P.* 134103, 1901; J. Hargreaves and T. Robinson, *Brit. Pat. No.* 508, 1872; W. Carpmael, *ib.*, 293494, 1927; H. N. Warren, *Chem. News*, **70**. 102, 1894; A. Burger, *Reduktion durch Calcium*, Basel, 7, 1907; V. H. Rochrich and E. V. Manuel, *Journ. Amer. Chem. Soc.*, **32**. 178, 1910; H. Kopp, *Liebig's Ann. Suppl.*, **3**. 294, 1865; M. Faraday, *Phil. Trans.*, **136**. 21, 41, 1846; L. F. Nilson and O. Pettersson, *Oefvers. Handl. Stockholm*, 6, 1880; *Chem. News*, **43**. 17, 1881; *Proc. Roy. Soc.*, **31**. 46, 1881; *Ber.*, **13**. 1465, 1880; L. Gattermann, *ib.* **22**. 197, 1889; W. N. Hartley, *Phil. Trans.*, **185**. A, 161, 1894; *Proc. Roy. Soc.*, **54**. 5, 1893; *Chem. News*, **67**. 279, 1893; I. L. Bell, *ib.*, **23**. 258, 1871; L. Elsner, *Die chemisch-technischen Mitteilungen*, Berlin, 36, 1858; H. Collins, *Chem. News*. **132**. 262, 1926; H. le Chatelier, *Bull. Soc. Chim.*, (2), **47**. 303, 1887; L. Godefroy, *ib.*, (2), **40**. 168, 1883; E. A. Werner, *Proc. Chem. Soc.*, **22**. 257, 1906; J. Parkinson, *Journ. Chem. Soc.*, **20**. 309, 1867; H. C. Greenwood, *ib.*, **93**. 1488, 1908; L. Playfair and J. P. Joule, *Mem. Chem. Soc.*, **3**. 82, 1848; F. Ephraim, *Zeit. anorg. Chem.*, **44**. 193, 1905; J. Milbauer, *ib.*, **42**. 442, 1904; G. Rothaug, *ib.*, **84**. 165, 1913; W. Guertler, *ib.*, **40**. 226, 1906; R. Schwarz, *Helvetica Chim. Acta*, **3**. 330, 1920; K. Endell and R. Rieke, *Centr. Min.*, 246, 1914; K. Brückner, *Monatsh.*, **27**. 199, 1906; M. Z. Jovitschitsch, *ib.*, **30**. 47, 1909; R. D. Hall, *Journ. Amer. Chem. Soc.*, **26**. 1244, 1904; G. B. Frankforter, V. H. Roehrich and E. V. Manuel, *ib.*, **32**. 178, 1910; A. F. Benton, *ib.*, **45**. 887, 1923; W. P. Yant and C. O. Hawk, *ib.*, **49**. 1454, 1927; A. T. Cameron, *Proc. Roy. Soc. Edin.*, **25**. 733, 1905; J. J. Berzelius, *Schweigger's Journ.*, **16**. 405, 1814; **22**. 53, 1818; *Pogg. Ann.*, **1**. 34, 1824; *Ann. Chim. Phys.*, (2), **17**. 7, 1821; F. Göbel, *Bull. Soc. Nat. Moscow*, **9**. 312, 1836; *Journ. prakt. Chem.*, (1), **6**. 386, 1835; B. Neumann, *Stahl Eisen*, **28**. 356, 1908; *Zeit. Elektrochem.*, **14**. 169, 1908; P. Askenasy and C. Ponnaz, *ib.*, **14**. 810, 1908; L. and P. Wöhler, *Zeit. phys. Chem.*, **62**. 440, 1908; L. and P. Wöhler and W. Plüddemann, *ib.*, **62**. 641, 1908; L. Wöhler and M. Rabinowitsch, *Koll. Zeit.*, **38**. 111, 1926; L. Wöhler, *ib.*, **11**. 241, 1913; **38**. 97, 1926; L. Wöhler and J. Dierksen, *Zeit. angew. Chem.*, **39**. 13, 1926; P. Hausknecht, *Magnetochemische Untersuchungen*, Strassburg, 1913 ; A. S. Russell, *Phys. Zeit.*, **13**. 59, 1912 ; W. P. Davey, *Phys. Rev.*, (2), **21**. 716, 1923 ; R. Robl, *Zeit. angew. Chem.*, **39**. 608, 1926 ; R. Klemm, *Centr. Min.*, 267, 1927 ; D. Meneghini, *Gazz. Chim. Ital.*, **43**. i, 81, 1913 ; A. L. D. d'Adrian, *U.S. Pat. No.* 1429912, 1922 ; S. Veil, *Journ. Chim. Phys.*, **24**. 428, 1927 ; A. Löwenthal, *German Pat., D.R.P.* 239651, 1909 ; Anon., *Farbenztg.*, **32**. 1020, 1075, 1136, 1927 ; *Journ. Soc. Dyers Colorists*, **43**. 169, 1927 ; *Chem. Trade Journ.*, **80**. 529, 1927 ; A. E. Tschitschibabin, *Journ. Russ. Phys. Chem. Soc.*, **47**. 703, 1916 ; A. Fodor and A. Reifenberg, *Koll. Zeit.*, **42**. 18, 1927 ; R. Whytlaw-Gray, J. B. Speakman, and E. Thomson, *Nature*, **107**. 619, 1921 ; E. Thomson, *ib.*, **107**. 520, 553, 1921 ; T. Sabalitschka and F. Bull, *Zeit. anal. Chem.*, **64**. 322, 1924 ; A. Duboin, *Compt. Rend.*, **134**. 840, 1902 ; L. J. Simon, *ib.*, **175**. 768, 1922 ; L. Liechti and J. J. Hummel, *Journ. Soc. Chem. Ind.*, **26**. 736, 1922 ; H. Rheinboldt and E. Wedekind, *Koll. Beihefte*, **17**. 115, 1923 ; K. Skaupy, *Phys. Zeit.*, **28**. 842, 1927 ; W. D. Bancroft, *Journ. Phys. Chem.*, **26**. 736, 1922 ; H. H. Storch, *ib.*, **32**. 1743, 1928 ; A. W. Davison, *ib.*, **21**. 190, 1917 ; H. P. Cady and R. Taft, *ib.*, **29**. 1075, 1925 ; H. Schmidt-Reps, *Zeit. tech. Physik*, **6**. 322, 1925 ; H. Bodenbender, *Journ. Pharm. Chim.*, (4), **4**. 313, 1866 ; *Zeit. Zuckerind.*, **15**. 167, 1865 ; H. D. Rankin, *U.S. Pat. No.* 1471751, 1924 ; W. Eidmann, *Ein Beitrag zur Erkenntnis des Verhalten chemischer Verbindungen in nichtwässerigen Lösungen*, Giessen, 1899 ; J. Böhm, *Zeit. anorg. Chem.*, **149**. 217, 1925 ; E. Tiede and E. Birnbrauer, *ib.*, **87**. 129, 1914 ; L. Blanc, *Ann. Chim. Phys.*, (10), **6**. 182, 1926 ; *Étude de quelques transformations observées au cours de calcination des sesquioxydes de fer et de chrome et d'aluminium*, Paris, 1926 ; L. Blanc and G. Chaudron, *Compt. Rend.*, **182**. 386, 1926 ; G. Chaudron and H. Forestier, *ib.*, **179**. 763, 1924 ; E. Moles and F. Gonzalez, *Anal. Fis. Quim.*, **21**. 204, 1923 ; K. Fuwa, *Journ. Japan Cer. Soc.*, 192, 1923 ; T. Dreisch, *Zeit. Physik*, **40**. 714, 1927 ; E. Friederich, *ib.*, **31**. 813, 1925 ; G. H. Hurst, *Colour*, London, 46, 1900 ; R. Saxon, *Chem. News*, **132**. 310, 1926 ; H. von Wartenberg, J. Broy and R. Reinecke, *Zeit. Elektrochem.*, **29**. 214, 1923 ; F. Born, *ib.*, **31**. 309, 1925 ; V. Kohlschütter and J. L. Tüscher, *ib.*, **27**. 225, 1921 ; C. Zengelis, *Zeit. phys. Chem.*, **50**. 219, 1904 ; O. Schmidt, *ib.*, **133**. 263, 1928 ; H. S. Patterson and R. Whytlaw-Gray, *Proc. Leeds Phil. Lit. Soc.*, **1**. 70, 1926 ; R. E. Slade and G. I. Higson, *B.A. Rep.*, 450, 1913 ; K. Chakravarty and S. C. Ghosh, *Journ. Indian Chem. Soc.*, **4**. 431, 1927 ; H. Hagaoka and T. Futagami, *Proc. Acad. Tokyo*, **3**. 643, 1927 ; H. N. Warren, *Chem. News*, **55**. 155, 1887 ; W. A. Lazier, *U.S. Pat. No.* 1746781, 1930 ; V. V. Polyansky, *Trans. Inst. Pure Chem. Reagents*, 300, 1929 ; R. Wasmuth, *Zeit. angew. Chem.*, **43**. 98, 125, 1930 ; G. Liebmann, *Zeit. Physik*, **63**. 404, 1930 ; M. Siewert, *Zeit. ges. Naturwiss.*, **18**. 244, 1861 ; J. Vrede, *Phys. Zeit.*, **31**. 323, 1930 ; E. Newberry and J. N. Pring, *Proc. Roy. Soc.*, **92**. A, 276, 1916 ; L. Passerini, *Gazz. Chim. Ital.*, **60**. 544, 1930 ; H. von Wartenberg and H. Werth, *Zeit. anorg. Chem.*, **190**. 178, 1930 ; P. E. Wretblad, *ib.*, **189**. 329, 1930 ; J. Maydel, *ib.*, **186**. 289, 1930 ; W. Biltz, A. Lemke and K. Meisel, *ib.*, **186**. 373, 1930 ; O. Ruff and H. Krug, *ib.*, **190**. 270, 1930 ; E. N. Bunting, *Journ. Research Bur. Standards*, **5**. 325, 1930 ; E. H. Humphries, *Canada Pat. No.* 303455, 1930 ; E. Wydler, *French Pat. No.* 685193, 1929 ; A. Kutzelnigg, *Ber.*, **63**. B, 1753, 1930 ; W. A. Roth and G. Becker, *Zeit. phys. Chem.*, **145**. 461, 1929 ; K. Fredenhagen and G. Cadenbach, *ib.*, **146**. 245, 1930 ; J. R. Huffmann and B. F. Dodge, *Journ. Ind. Eng. Chem.*, **21**. 1056, 1929 ; W. E. Garner and F. E. T. Kingman, *Nature*, **126**. 352, 1930.

§ 10. Hydrated Chromium Oxides. Chromium Hydroxide

Some of the *chrome ochres*—**6**. 40, 49—contain hydrated chromic oxide. According to W. Ipatieff and A. Kisseleff,[1] if $2N$-H_2CrO_4 at 240°–300° be exposed to hydrogen at 150° to 180° atm. press., a heavy, greyish-violet, slightly crystalline precipitate of **chromic oxyhydroxide,** $Cr_2O_3.H_2O$, or $CrO(OH)$, is formed ; if in 25 c.c. of soln., 4 c.c. of $\frac{1}{10}N$-H_2SO_4 be present, in a gold tube, a similar violet-grey precipitate is formed at 300° to 325° ; and in a quartz tube, the crystals are green, and cubic. If more sulphuric acid is present, at 300°, and 180 to 200 atm. press., two kinds of crystals are formed. According to W. Ipatieff and B. Mouromtseff, a nitric acid soln. of chromic nitrate when exposed to hydrogen at 320°–360°, under a press. of 200–370 atm., for 12–24 hrs., gives monohydrated chromium oxide closely resembling chrome ochre. If air is used in place of hydrogen, smaller crystals are obtained and the separation is not quantitative, a portion of the oxide being converted into chromic acid. Small amounts of dark red crystals are also occasionally obtained. According to J. B. Trommsdorff, if soln. of chromic salts are treated with alkali hydroxides, or aq. ammonia, it is best to work with boiling soln. It is difficult to wash the precipitated hydrated chromic oxide free from adsorbed salts. The product has been called **chromic hydroxide,** $Cr(OH)_3$, but it is generally supposed to be a colloidal hydrated oxide of less definite composition. O. Ruff and B. Hirsch studied the fractional precipitation of chromic hydroxide in the presence of salts of other metals. S. Hakomori said that the reason ammonia does not precipitate hydrated chromic oxide in the presence of tartaric acid is because a complex salt is formed; and not in the presence of glycerol, because of colloidal phenomena induced by the high viscosity of the soln. The complex tartrate-ions were studied by K. Jellinek and H. Gordon.

J. J. Berzelius obtained a similar product by boiling a mixed soln. of potassium chromate and pentasulphide; G. F. C. Frick, by boiling a soln. of potassium chromate with sulphur; G. Lösekann, by the action of hydrogen sulphide on an alkaline soln. of a chromite oxide; H. Baubigny, by the action of hydrogen sulphide on a soln. of potassium dichromate; J. Casthelaz and M. Leune, by the action of zinc hydroxide, carbonate, or sulphide, or of aluminium hydroxide, or of zinc in a feebly acid soln. of green chromic chloride; and K. Seubert and A. Schmidt, by the slow action of magnesium on a warm soln. of a chromic salt. P. A. Thiessen and B. Kandelaky prepared the hydroxide free from adsorbed electrolytes by the hydrolysis of chromic ethylate: $2Cr(OC_2H_5)_3+6H_2O=Cr_2O_3.3H_2O+6C_2H_5OH$. A. Simon and co-workers used P. A. von Bonsdorff's process for hydrated alumina, and treated a soln. of the hydroxide in soda-lye with freshly precipitated, hydrated oxide, and after washing with water, and drying with acetone obtained a product with $Cr_2O_3.5{\cdot}68H_2O$. B. Schwarz obtained the hydroxide by the hydrolysis of chromites. V. Ipatéeff produced crystals of the hydrated oxide by heating soln. of the salts at high temp. and press. A. C. Becquerel obtained crystals of the hydroxide by suspending a parchment paper tube containing a conc. soln. of potassium aluminate in a soln. of chromic chloride. J. Férée obtained what he regarded as a monohydrate $Cr_2O_3.H_2O$, or $Cr(OH)O$, as a black, amorphous powder by the electrolysis of a neutral soln. of chromic chloride with a platinum cathode. This subject has been previously discussed in connection with R. Bunsen's, and J. Voisin's observations on the electro-deposition of chromium. G. B. Frankforter and co-workers heated a mixture of potassium dichromate and ammonium chloride to 260° and obtained a slate-coloured residue which, on lixiviation with water, left small, greenish-black, iridescent spangles of what has been thought to be a *dihydrate*, $Cr_2O_3.2H_2O$, or $Cr_2(HO)O$.

Analyses of the hydrates of chromic oxide vary very much. According to M. Siewert, the precipitate which has stood for some hrs. in air at 45° for 3 hrs. has $5{\cdot}9\ H_2O$; 3 hrs. at 100°, $5{\cdot}2H_2O$; 4 hrs. at 100°, $4{\cdot}8H_2O$; 2 hrs. at 105°, $4{\cdot}2H_2O$; 2 hrs. at 150°, $3{\cdot}2H_2O$; 5 hrs. at 200°, $2{\cdot}3H_2O$; and 6 days at 220°, $1{\cdot}1H_2O$. L. Schaffner obtained for the ammonia-precipitate dried over sulphuric acid, $6H_2O$; and dried at 100°, $5H_2O$; the alkali-precipitate dried at 100°, $4H_2O$. A. J. W. Forster gave for the air-dried, ammonia-precipitate $Cr_2O_3.8H_2O$. E. Frémy found for the potash-precipitate obtained in the cold, and dried in air, $9H_2O$, and that obtained from a boiling soln., and dried in air, $8H_2O$. J. Lefort, and A. Schrötter obtained similar data. C. F. Cross represented the composition of the precipitate dried at 100° by $Cr_2O_3.4H_2O$, and after standing in air sat. with moisture, $Cr_2O_3.7H_2O$, and after heating to dull redness, $Cr_2O_3.3H_2O$. M. Prud'homme gave $Cr_2O_3.5H_2O$ for the precipitate dried at 100°. G. Wyrouboff gave $Cr_2O_3.8H_2O$ for the precipitate dried over sulphuric acid, and $Cr_2O_3.6H_2O$ when dried at 110°. According to H. Löwel, the red-coloured ammonia-precipitate which dissolves in ammonia forming a red soln. is a different hydroxide from the bluish violet-coloured hydroxide, and this again is different from the green-coloured hydroxide. J. Lefort, E. Frémy, and J. M. Ordway also regarded the differently coloured hydroxides as isomers. According to A. Recoura, chromic hydroxide exists in three different molecular conditions. The first is obtained by precipitating a soln. of either variety of chromic chloride or of any violet chromium salt with an eq. quantity of sodium hydroxide. If treated with hydrochloric acid immediately after precipitation, it combines with 6 mols. of HCl with the development of 41·4 cals. The second variety is obtained by precipitating the oxychloride Cr_2Cl_4O

with 4 mols. of sodium hydroxide. Immediately after precipitation, it combines with 4 mols. of hydrochloric acid only, with development of 24·2 cals. The subsequent addition of a further quantity of 2 mols. of acid produces no thermal disturbance. The third form is obtained when either of the preceding varieties is dissolved in the necessary excess of soda-lye (18 mols. in the first case, 6 mols. in the second), and reprecipitated by neutralizing the excess of alkali. It combines with only 4 mols. of hydrochloric acid, with development of 20·0 cals. A. Colson assumed that there are hydroxides corresponding with the green and violet sulphates. He supposed that the green sulphate corresponded with

$$\begin{array}{c}(\mathrm{OH})_2{=}\underset{\cdot}{\mathrm{Cr}}{-}\mathrm{O}{-}\underset{\cdot}{\mathrm{Cr}}{=}(\mathrm{OH})_2\\ (\mathrm{OH})_2{=}\mathrm{Cr}{-}\mathrm{O}{-}\mathrm{Cr}{=}(\mathrm{OH})_2\end{array}$$

This formulation for hydrated chromic oxide—*i.e.* $Cr_4(OH)_8O_2.10H_2O$, or $Cr_4(OH)_{10}{\cdot}0{\cdot}9H_2O$—was favoured by M. Z. Jovitschitsch. G. Wyrouboff supposed the violet hydroxide is constituted $Cr_2(OH)_6$, and the other hydroxide $Cr_2(OH)_4(OH)_2$, or $Cr_2O(OH)_2$, where the two OH-groups can function as an acid. Although J. J. Berzelius assumed that the oxides precipitated from violet and green soln. of chromic chloride are isomers because they gave the soln. the original colour when dissolved in acids, yet the observations of A. Recoura indicate that the hydrated oxides from differently coloured soln. are the same in chemical structure. The individual variation depends on differences in the physical character of the particles. The rate of precipitation was shown by J. Casthélaz and M. Leune, and H. B. Weiser to have a marked effect on the colour. When slowly precipitated, the oxide is dark green and granular, and when rapidly precipitated greyish-blue and gelatinous. P. Bary and J. V. Rubio found that the dried hydroxide is heterogeneous, for it contains two products. R. Fricke and F. Wever could detect no evidence of crystal structure by X-radiograms.

N. Bjerrum measured the potential of the hydrogen electrode immersed in soln. of chromic chlorides, and inferred that the violet chromic chloride is progressively hydrolyzed, $CrCl_3 \rightarrow CrCl_2(OH) \rightarrow Cr(OH)_2Cl \rightarrow Cr(OH)_3$. He considered that freshly precipitated chromic hydroxide, $Cr(OH)_3$, is a well-defined chemical compound with a solubility product of $4{\cdot}2\times10^{-16}$ at 0° and $5{\cdot}4\times10^{-16}$ at 17°. On the other hand, J. M. van Bemmelen observed that the bluish colloid, prepared by treating a dil. soln. of a chromic salt with ammonia at the ordinary temp. or at 100°, contains originally 11 mols. H_2O; after exposure to the air at 15° it contains 7·8 to 8 mols.; but after keeping for 14 days in an atm. sat. with moisture the quantity of water rises to 13·2 mols., and after exposure to dry air it falls to 7·0 mols. When heated in the air at temp. increasing from 45° to 200°, the amount of water falls from 5·9 to 2·3 mols., and the colour changes to a dirty green. The results obtained on heating at temp. varying from 15° to 100° (i) in a sat. atm., (ii) in ordinary air, and (iii) in dry air, until the weight is constant, show that at every temp. equilibrium is established between the vap. press. of the colloid and that of water at the same temp. At 65° and at 100°, it retains more water in a sat. atm. than at 15° and 65° respectively in a dry atm. After having been heated at from 15° to 100° in dry air, its absorptive power is only slightly diminished, and at higher temp. it retains more water than colloidal silica, alumina, stannic acid or ferric oxide at the same temp., but the higher the temp. to which it has been exposed, the more insoluble it becomes in acids and especially in alkalies. He therefore inferred that colloidal chromic oxide has no definite composition at any temp. between 15° and 280°. This conclusion was confirmed by A. L. Baykoff, and H. B. Weiser. R. Fricke examined the X-radiogram of the hydroxide. S. Veil studied the effect of chromic hydroxide on the decomposition of hydrogen dioxide. H. J. S. King prepared **chromic pentamminohydroxide,** $Cr(OH)_3.5NH_3$, or **chromic hydroxypentamminohydroxide,** $[Cr(NH_3)_5(OH)](OH)_2$, by triturating chromic chromopentamminochloride with moist silver oxide, as indicated by O. T. Christenson. Similar results were obtained by using chromic aquopentamminochloride.

L. Havestadt and R. Fricke studied the dielectric constant. The electrical conductivity, μ mhos, for soln. with a mol of the salt in v litres of water at 0°, and the calculated percentage degree of ionization, α, are :

v . .	22·53	32·85	42·92	65·70	365·8	∞
μ . .	237·8	245·5	250·0	254·1	273·7	283·9
α . .	83·8	86·5	88·1	89·5	96·4	

Hydrated chromic oxide can be obtained in various shades of colour ranging from a clear greyish-blue to a dark green. Some of these are utilized as permanent pigments. The so-called *Guignet's green* has attracted some attention. This vivid, green pigment was prepared by E. Guignet by heating a mixture of potassium dichromate with three times its weight of boric acid, digesting the product with water, and washing it with water. Modifications of the process were described by A. Salvétat, M. Poussier, and A. Scheurer-Kestner ; L. Wöhler and W. Becker, in agreement with A. Scheurer-Kestner, said that boron is without influence on the colour, and that the trace of boron present is derived from the chromium borate first formed and subsequently hydrolyzed. If ammonium dichromate is employed in place of potassium dichromate, not a trace of boron remains after the washing, and when dried at 110°, the product has the composition $2Cr_2O_3.3H_2O$, or $Cr_4O_3(OH)_6$, ascribed to it by A. Scheurer-Kestner, and E. Guignet. A. Salvétat gave $Cr_3O_3.2H_2O$; A. Eibner and O. Hue, $2Cr_2O_3.5H_2O$; and M. Shipton considered it to be a borate, $3Cr_2O_3.B_2O_3.4H_2O$. According to L. Blanc, Guignet's green is not a hydrate, but very finely-divided chromic oxide, which, when heated in air, or treated with chromic acid, forms β-Cr_5O_9. L. Wöhler and J. Dierksen observed that when the green is produced by fusing potassium dichromate with boric acid, the failure to convert the dull olive-green to the brilliant green pigment by heating with water under press. supported the view that the complex $Cr_2O_3.3B_2O_3$ is responsible for the colour, but boric oxide is not a necessary constituent of the bright green. They suggest that the bright green has a gel-structure ; X-radiograms show that a lattice structure is absent. The reduction of the amount of water in chromium hydroxide gels with an increase in the size of particles progressively increases the brilliancy of the product. Boric acid and silicic acid are effective in producing the required flocculation. The vap. press. of brilliant flocculated hydroxides is greater than that of the dull non-flocculated hydroxides of the same water-content. L. Blanc and G. Chaudron found that Guignet's green yields a black oxide, Cr_5O_9, when heated. L. Wöhler and W. Becker said that a green pigment resembling Guignet's green can be obtained by heating the ordinary oxide with water under press. at 180° to 250°. The composition approximates $2Cr_2O_3.3H_2O$. Whilst Guignet's green has a vap. press. of 13 mm. at 75°, 16 mm. at 81°, and 26 mm. at 86°, the greyish-violet chromium hydroxide, which has the same composition, is found to have a vap. press. of only 2 mm., not increasing between 75° and 93·4°. This small vap. press. may result from the presence of moisture. These differences and the difference in colour of the two hydrates are ascribed to isomerism. The greyish-violet hydroxide is converted into its brilliant green isomeride on prolonged heating with water at 250°. H. B. Weiser added that the amorphous, hydrated oxide, obtained by precipitation, loses water continuously, and while it may be possible to dry the pigment under conditions such that the composition may be expressed by a single formula, yet this does not prove that a true hydroxide is formed. There is no evidence of an inversion temp. in the passage from one coloured variety to that of another colour ; and H. B. Weiser observed that when a soln. of chromic chloride is treated with just enough sodium hydroxide for complete precipitation the precipitate obtained at 0° is greyish-blue ; that at 50°, greenish-blue ; that at 100°, bluish-green ; that at 150°, green with a bluish tinge ; that at 200°, clear green ; and that at 200°–325°, bright green. The time of heating was 30 min. except in the last case when the heating occupied 15 hrs. Hence the colour varies continuously from greyish-blue to clear green as the temp. of precipitation rises; this shows that the colours are not due to isomers, but rather to differences in the sizes of the particles, the structure of the mass, and to the amounts of water enclosed under different conditions of formation. As the temp. of precipitation rises, the oxide becomes less gelatinous, less soluble in acids, and less readily peptized by alkalies. For the solubility of chromic hydroxide in alkali-lye, *vide infra*, chromites.

Hydrated chromic oxide freshly precipitated from cold soln. of a chromic salt by an alkali hydroxide or ammonia, is readily soluble in acids, and readily peptized by alkali hydroxides. The hydrated oxide, however, gradually suffers a change in physical character on *ageing*, and it then becomes far less soluble and far less chemically active. The process of ageing is attended by the growth of aggregates of the primary colloidal particles. The velocity of change is accelerated by raising the temp., or by the use of a medium with a slight solvent action. A. Recoura measured the molar heat of soln. in hydrochloric acid with an oxide precipitated by adding an acid to a colloidal soln. in alkali-lye, and kept for definite intervals of time. Thus, the mol. ht. of soln. in cals. of the freshly precipitated oxide is 20·70; when kept 10 min., 19·0 cals.; 1 hr., 5·80 cals.; 2 hrs., 3·90 cals.; 4 hrs., 2·85 cals.; 7 hrs., 2·40 cals.; 1 day, 1·75 cals.; 7 days, 1·20 cals.; 30 days, 0·75 cal.; and 60 days, 0·50 cal. F. Bourion and A. Sénéchal observed that the rate at which hydrated chromic oxide reduces hydrogen dioxide becomes less on standing. The reaction appeared to be quadrimolecular for the first 8 hrs., due, it was supposed, to the transformation of the original oxide into complexes, so that the soluble and insoluble varieties represent definite allotropic forms. R. Fricke and O. Windhausen attributed the ageing to an increase in the size of the particles, and showed that it is not due to dehydration, or to the development of a microcrystalline structure. R. Fricke and co-workers observed no evidence of a crystalline structure in the ageing of hydrated chromic oxide. A. Simon and co-workers studied the vap. press. of the hydrated oxide. The continuous curve, Fig. 17, was obtained with a preparation precipitated by ammonia, washed with water at 60°, then with acetone, and dried in air. Its composition approximated $Cr_2O_3.6{\cdot}68H_2O$. This curve shows a slight flattening with the tri- and mono-hydrate. The other curve is obtained with a specimen precipitated by hydrazine, washed, and dried over sulphuric acid in vacuo for 8 weeks when its ocmposition was $Cr_2O_3.4{\cdot}87H_2O$. The formation of the tri- and mono-hydrates is clearly shown.

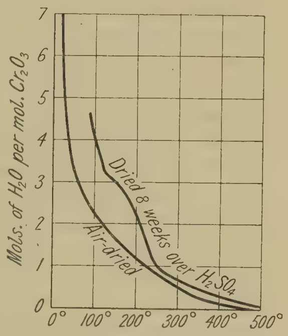


FIG. 17.—The Vapour Pressure of Hydrated Chromic Oxides.

M. Siewert showed that when the hydrated oxide is heated to 200°, in air, it takes up oxygen forming a black powder of variable composition, and it is regarded as a mixture of chromic oxide, chromic anhydride, and water. M. Krüger first observed the tendency of the hydrated oxide to take up oxygen when heated. A. Geuther showed that when the hydrated oxide is deposited on the negative pole, it is liable to form chromic anhydride by taking up oxygen. M. Z. Jovitschitsch found that hydrated chromic oxide readily absorbs carbon dioxide from the atm. forming $[Cr_2(OH)_5]_2CO_3.8H_2O$. The light grey hydrated chromic oxide which is precipitated with small quantities of ammonium hydroxide dissolves in an excess of ammonia to form a ruby-red soln. whose solubility is affected by the presence of ammonium salts. If the red soln. is kept for some time, M. Z. Jovitschitsch observed that violet-blue **chromium diamminohydroxide,** $Cr_2(OH)_6.(NH_3)_2.10H_2O$, is precipitated; it readily absorbs carbon dioxide.

A. Recoura gave for the heat of neutralization of hydrated chromic oxide with hydrochloric acid $\frac{1}{3}Cr(OH)_3=6{\cdot}865$ Cals.; E. Petersen, with hydrofluoric acid, 8·39 Cals.; and M. Berthelot, with sulphuric acid, $\frac{1}{2}H_2SO_4$, 8·22 Cals. W. Pauli and E. Valko studied the conductivity and activity coeff. H. R. Robinson and C. L. Young studied the absorption frequency of the K-series of X-ray spectrum. L. Havestadt and R. Fricke studied the dielectric behaviour of the hydroxide; and H. R. Robinson and C. L. Young, the X-ray absorption frequencies. F. Bourion and A. Sénéchal found that the paramagnetism of an alkaline soln. of chromic oxide diminishes slowly with time, but the diminution is small, and never exceeds 20 per cent. S. Veil found that the magnetic properties of chromic hydroxide are decreased by heating it with water in a sealed tube between 120° and 210°; and another 12 hrs.' treatment has little effect, but when the hydroxide is dissolved in hydrochloric acid, and reprecipitated, the modified magnetism persists and a further change occurs by a similar treatment with hot water. T. Ishiwara found the magnetic susceptibility at 15·7° to be $66·2\times10^{-6}$ mass units, and at $-68·3°$, $110·5\times10^{-6}$ mass units. P. Hausknecht, and E. Wedekind and W. Albrecht observed that the magnetic susceptibility of $Cr(OH)_3$ is greater than that of the corresponding oxide, in agreement with the assumption that the hydroxide is a chemical individual. S. Veil found that the magnetic properties of chromic hydroxide fall to a lower limiting value on repeated precipitation from hot soln.

T. Graham prepared a positive **colloidal solution** of hydrated chromic oxide by peptizing the freshly precipitated oxide with chromic chloride, and dialyzing the liquid to remove the excess of electrolyte. The dark green soln. can be diluted with water or heated, but it is readily flocculated by electrolytes. In continuous dialysis, the diffused liquid was kept at a constant level and not changed during the process, whereas in intermittent dialysis, the diffusate was continuously changed at the rate of 800 c.c. per hour. M. Neidle and J. Barab found that some colloidal particles do diffuse through the parchment membrane; although W. Biltz, and H. W. Fischer and W. Herz observed no such diffusion. In the dialysis of hydrated chromic oxide in a soln. of chromic chloride, the ratio $\frac{1}{3}Cr : Cl$ in the diffusate, with intermittent dialysis, is always greater than unity, and this the more the longer the period of dialysis for the same diffusate. In continuous dialysis, the ratio $\frac{1}{3}Cr : Cl$ in the diffusate increases from unity to a maximum of 1·57, and then gradually diminishes towards zero. In intermittent dialysis, about 6 per cent. of the original colloid is still associated with considerable electrolyte, and it remains in the membrane at the end of 56 days; but the colloid still diffuses so that by continuing the process, the whole of the colloid would be removed from the membrane. In the continuous dialysis, 75 per cent. of the original colloid remains in the membrane. Continuing the process for 35 days increases the purity of the colloid without loss of chromium. If the intervals in intermittent dialysis are made smaller, more satisfactory results are to be expected. In fact, by conducting the entire process in very short intervals, the efficiency may even exceed that of continuous dialysis. The latter procedure is, however, impractical. The variations in the ratio of $\frac{1}{3}Cr : Cl$ in the diffusates are accounted for by the assumption of a gradual growth of the particles. In the intermittent process, the particles do not grow sufficiently to be retained by the membrane, whereas in the continuous process they do. A. Simon and co-workers used the dialyzer recommended by A. Gutbier and co-workers. The process of dialysis was studied by N. Bjerrum by measuring the osmotic press. of the colloidal soln. It is hence calculated that the colloidal chromium particle consists of 1000 chromium atoms and carries 30 free charges. The number of chromic oxide molecules in a colloidal particle is about 240. For complete coagulation the necessary amount of ferrocyanide corresponds exactly with the total charge on the colloid, whilst about 15 per cent. excess of ammonium or potassium sulphate is required. The commencement of coagulation is marked by a sudden break in the curve obtained by plotting conductivity against c.c. of ammonium sulphate. The subject was discussed by A. Lottermoser and W. Riedel, and H. Rinde. R. Wintgen and W. Biltz gave 580 for the number of chromic oxide molecules in a colloidal particle aged by boiling, and 750,000 for the case of an aged ferric oxide colloidal particle. These numbers are of doubtful accuracy. J. R. I. Hepburn found that the product obtained after a prolonged freezing is colloidal in nature, but has some properties usually regarded as characteristic of the crystalline state. J. H. Yoe and E. B. Freyer measured the $H^{\cdot}$-ion conc. and viscosity of hydrosols of chromic oxide; D. N. Chakravarti and N. R. Dhar, the viscosity of the sol in the presence of electrolytes; E. Manegold and R. Hofmann, the permeability of membranes for the hydrosol; and S. Horiba and H. Baba, the effect of light on the osmotic pressure of the hydrosol.

C. Paal prepared a colloidal soln. of hydrated chromic oxide by reducing a soln. of ammonium chromate with colloidal platinum in the presence of sodium protalbinate which acts as a protective colloid. The colloid may be partially purified by dialysis. Soln. of aluminium or ferric salts give a precipitate of hydrated oxide when boiled with sodium acetate; but with chromic acetate soln., H. Schiff, and B. Reinitzer obtained no precipitate when the soln. was boiled; nor was a precipitate obtained in the cold with alkali hydroxide, ammonia, ammonium hydroxide or carbonate, sodium phosphate, or with barium hydroxide or carbonate. Except in the case of sodium phosphate, these reagents give precipitates with boiling soln. There is a slow action between chromic salt and sodium acetate in the cold, for, on standing some time, in the presence of alkali, the colour of the liquid changes and a jelly is formed. In the case of a boiling soln. of hydrated chromic oxide and sodium acetate, the precipitate formed is probably a complex acetate. Iron and aluminium acetates associated with violet chromic acetate do not give a precipitate when boiled or when treated with alkali-lye or aq. ammonia. This, said H. B. Weiser, is not due to peptizing action of the adsorbed hydrated chromic oxide because hydrated chromic oxide is not the primary product of the hydrolysis of chromic acetate, and, as B. Reinitzer has shown, green chromic acetate does not prevent the precipitation of hydrated ferric oxide. The phenomenon as probably the result of the formation of the iron-chromic acetates was studied by R. F. Weinland and E. Guzzmann. The alleged formation of colloidal hydrated chromic oxide, by B. Reinitzer and H. W. Woudstra, by dialyzing soln. of chromic acetate, does not seem right since basic chromic acetates are probably produced. M. Neidle and J. Barab obtained no colloid by dialyzing chromic acetate soln. into which superheated steam was passed; nor was any obtained by the dialysis of a cold soln. of purified chromic chloride, although H. M. Goodwin and F. W. Grover obtained a little by the dialysis of the commercial ferric chlorides. W. Biltz obtained no colloid by the hydrolysis of soln. of chromic nitrate, owing to the small hydrolysis of the salt as observed by H. W. Woudstra. S. Takegami obtained the colloid at the cathode during the electrolytic reduction of chromic acid; and B. Kandelaky, by the hydrolysis of chromic ethylate.

H. W. Fischer studied the solubility of hydrated chromic oxide in a soln. of chromic chloride; R. Wintgen and H. Weisbecker, the amphoteric properties of the colloid; and P. Bary and J. V. Rubio, E. Manegold and R. Hofmann, and R. Wintgen and O. Kühn, the structure of the colloid. F. Haber showed that if the rate of aggregation of a colloidal sol is high, amorphous precipitates are to be expected which gradually, and particularly on warming, pass into the crystalline condition. If, however, the rate of aggregation is depressed by only slightly exceeding the solubility limit, the rate of arrangement may be sufficient to cause the orderly formation of crystals before the formation of visible particles has occurred. This, however, involves an alteration in the rate of aggregation due to electrical phenomena at the boundary of the molecules and liquid, the net result of which is that the growth of the aggregates is greatly impeded and sols are produced.

The colloidal soln. of hydrated chromic oxide prepared as just indicated was shown by W. Biltz, and W. Herz to be a **positive hydrosol** because it migrates to the cathode under the influence of an electrical stress. On the other hand, the green colloidal soln. obtained by adding an excess of alkali hydroxide to a soln. of a chromic salt was found by R. Kremann to be a **negative hydrosol** because, under the influence of an electrical stress, it migrates to the anode. W. Reinders studied the electrophoresis of the colloid. The clear, negative colloidal soln. was found by H. W. Fischer and W. Herz to precipitate spontaneously on standing, particularly if the ratio of chromic oxide to hydroxide is large. This is due to the ageing of the hydrated oxide. A. Hantzsch also observed that owing to ageing, the precipitated and washed chromic oxide is not peptized by alkalies. The colloid is precipitated by adding electrolytes owing to the adsorption of the cations as observed by H. W. Fischer. A. Lottermoser found that the ultra-filtration of the chromic oxide sol peptized with the corresponding chloride gives a filtrate which contains hydrochloric acid of the same $H^{\cdot}$-ion conc. as that of the sol. The mycellia therefore retains the chloride ion whose negative charge compensates the positive charge of the colloidal particles. The conductivity of the sol is greater than that of the ultra-filtrate, and the difference is taken to represent the true conductivity of the mycelles which are regarded as complex electrolytes. A. B. Dumansky and co-workers studied this subject. R. Fricke and co-workers found tetramethylammonium hydroxide to be a strong peptizing agent.

C. F. Nagel, W. D. Bancroft, and N. G. Chatterji and N. R. Dhar showed that the colloidal oxide can be removed by the ultra-filter. W. Biltz and W. Giebel added that the colloidal soln. consists mainly of amicrons, only a small proportion of sub-microns are present. There has been some discussion as to whether the colloidal soln. contains alkali chromite. H. W. Fischer and W. Herz said that peptization, not dissolution, occurs. This is in agreement with hypothesis that the soln. is really the colloidal oxide and the observation of A. B. Northcote and A. H. Church that complete soln. occurs in the presence of 40 per cent. of ferric oxide; 12·5, manganous oxide; or 20 per cent. of either cobalt or nickel oxide, whereas complete precipitation occurs with 80 per cent. of ferric oxide; 60, of manganous oxide; or 50, of either cobalt or nickel oxide. Analogous observations were made by M. Prud'homme, and M. Kreps. H. B. Weiser and G. L. Mack obtained an **organosol** in propyl alcohol.

According to C. F. Nagel, when an excess of potassium hydroxide is added to a soln. containing varied proportions of ferric chloride and chromic sulphate, the iron is not precipitated in presence of excess of the chromic salt, and the chromium is completely precipitated with the iron when the ferric salt is present in considerable excess. It is supposed that these effects are due to mutual adsorption. In a similar way, the hydroxides of manganese, cobalt, nickel, copper, and magnesium are absorbed by colloidal chromic hydroxide, whilst this is also adsorbed and removed from soln. by the above hydroxides when these are present in relatively large quantities. In presence of copper, chromium is not precipitated by ammonia, and it is suggested that this may be due to the presence of colloidal cupric hydroxide, which adsorbs the chromic hydroxide. The peptized soln. gradually settles leaving only a faintly coloured liquid; a collodion filter removes all the hydrated oxide leaving in soln. a little chromic chloride; and peptized hydrated chromic oxide cannot be extracted from soln. with benzene or light petroleum, but it goes into the dimeric interface. J. K. Wood and V. K. Black treated precipitated chromic oxide with varying proportions of a soln. of alkali hydroxide of varying concentration. The presence of chromate in the soln., after two months, indicated that some chromite had been formed; whilst a soln. of chromic chloride treated with a large excess of alkali-lye, after standing two months, gave a colloidal precipitate, and a yellow soln. of chromate formed by oxidation. They concluded that chromites do exist in an alkaline soln. of chromic hydroxide; when the soln. is freshly prepared and is kept a little time, part of the dissolved hydroxide separates out in a less soluble form, and probably does, during this period of transition, exist for a time in the colloidal condition, but when all such precipitation has taken place, a small amount of chromite will still be present in the soln.

According to E. Müller, when an excess of chromic oxide or hydroxide is shaken with aq. soln. of sodium hydroxide for several days, the solubility is dependent on the time of agitation, rising to a maximum and then falling to a constant value. Both the maximum and final solubilities attain their highest values at 14N-NaOH. It is assumed that chromium hydroxide is a "solid-liquid" in which simple and polymerized molecules are present in homogeneous soln. On account of the magnitude of the internal friction, equilibrium is only slowly attained. The ageing process does not so much consist in the enlarging of single particles as in a progressive change during polymerization and is thus essentially chemical in character. H. B. Weiser added that even if chromic oxide does possess slightly acidic properties, not all the oxide is present as chromite; and it is doubtful if any chromite is present when slightly more alkali-lye is present than is needed to precipitate the chromic oxide completely. H. N. Holmes and M. A. Dietrich observed that mercuric sulphide is not precipitated by hydrogen sulphide from a 0·5N-hydrochloric acid soln. containing green chromic chloride and mercuric chloride in excess of the ratio 2 : 1, but is adsorbed by the colloidal chromic hydroxide produced by the hydrolysis of the chloride. The hydrolysis increases on keeping, and after 48 hrs. precipitation does not occur when the above ratio is 1 : 3·5, but this ratio may be depressed by a sufficient concentration of hydrogen or sulphate ions. Thus, chromic sulphate has no influence on the precipitation. The formation of colloidal chromic hydroxide is probably preceded by the conversion of the green chromic chloride into the violet form. The order of the adsorption is reversed by using a large excess of mercuric chloride and precipitating from a hot 0·5N-acid soln. K. C. Sen found that the absorption of acids by chromic oxide can be summarized in Fig. 18.

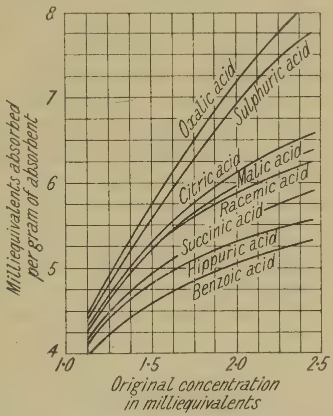


FIG. 18.—The Absorption of Organic Acids by Hydrated Chromic Oxide.

H. B. Weiser reported that the precipitation values for potassium salts for a negative colloidal soln. containing 365 grms. of chromic oxide per litre were for ferricyanide, 0·485 millieq. per litre; chromate, 0·525; dichromate, 0·535; sulphate, 0·550; oxalate, 0·570; iodate, 0·635; bromate, 19·0; chloride, 30·0; bromide, 33·0; chlorate, 33·8; and iodide, 37·5. M. Bjerrum observed that by adding a soln. of 0·1N-ammonium sulphate to a soln. containing 0·112 mols of Cr, and 0·01 mol of nitric acid, the electrical conductivity of the soln. altered as indicated in Fig. 19. E. E. Porter measured the H$^{\cdot}$-ion conc. of a negative colloidal soln. of hydrated chromic oxide containing 2·5 grms. Cr_2O_3 per litre, when 5 c.c. were treated with 15 c.c. of a soln. containing salt and acid. A rapid precipitation of the colloid occurred when the p_H was between 3·5 and 6·0. The flocculation of the colloidal soln. was also studied by A. Miolati and E. Mascetti, and N. Bjerrum, A. Ivanitzkaja and L. Orlova, S. L. Jindal and N. R. Dhar, K. Mohanlal and N. R. Dhar, W. V. Bhagwat and N. R. Dhar, S. Ghosh and N. R. Dhar, K. C. Sen and M. R. Mehrotra, K. C. Sen and N. R. Dhar, and R. Wintgen and H. Löwenthal. H. B. Weiser also studied the flocculation of a colloidal soln. of chromic oxide by mixed electrolytes; and for the precipitation value of a negative colloidal soln.

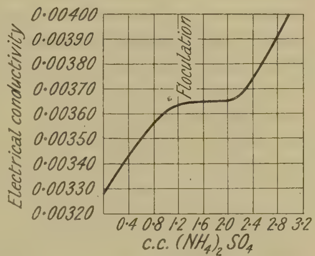


FIG. 19.—The Effect of Ammonium Sulphate on the Flocculation of a Colloidal Solution of Chromic Oxide.

obtained by adding 45 c.c. of $2N$-KOH to 5 c.c. of a soln. of chromic chloride containing 40 grms. of chromic oxide per litre, the result with barium chloride was 5·15 millieq. per litre; potassium chloride, 500·0; sodium chloride, 210·0; lithium chloride, 51·0; sodium sulphate, 315·0; and sodium acetate, 220·0. S. Roy and N. R. Dhar studied the coagulation of the colloid in light. T. Katsurai observed that the hydrosol of chromic oxide does not coagulate like that of ferric oxide when heated under press.

B. Reinitzer prepared a **hydrogel** by boiling a soln. of a chromic salt and sodium acetate, rendered alkaline by alkali-lye or ammonia, and allowing it to set to a jelly. E. H. Bunce and L. S. Finch obtained a jelly by allowing a mixed soln. of alkali-lye and chrome alum to stand. They did not get the jelly by using soln. of chromic sulphate, nitrate, or chloride; but C. F. Nagel obtained the jelly with sulphate by keeping down the conc. of the alkali. H. B. Weiser observed that the rapid addition of a slight excess of alkali-lye to a soln. of chromic chloride produces a negative colloidal soln. which precipitates slowly forming a jelly; if the precipitation is hastened by heating the soln., or by adding a suitable amount of electrolyte, the precipitation is rapid and it is gelatinous but not a jelly; and finally, if the hydrated oxide has been peptized by a large excess of alkali, the precipitate forms slowly and is granular. R. Griessbach and J. Eisele obtained the gel by peptizing the hydrosol. J. Häusler and B. Kohnstein obtained the gel by separately atomizing an acid soln. of chromic acid and an alkaline soln. of sucrose in a mixing chamber, and recovering the colloidal hydroxide. D. N. Chakravarti and N. R. Dhar found that during dialysis of a hydrosol of hydrated chromic oxide, the liquid becomes more viscid and finally gelatinizes. S. Prakash and N. R. Dhar found that the soln. of 4 c.c. $0·5M$-$CrCl_3$, and 8 c.c. of $3·57N$-$CH_3.COONa$, mixed in half an hour with 2 c.c. of $2N$-$(NH_4)_2SO_4$ and 5 c.c. of $2·34N$-NH_4OH added drop by drop, and the soln. made up to 20 c.c., sets to a jelly in 6½ hrs. at 30°. The viscosities of the soln. were:

Age . .	0	30	60	90	120	150 min.
Viscosity .	0·01465	0·01469	0·01527	0·01646	0·01873	0·02208

K. C. Sen and M. R. Mehrotra studied the peptization of chromic hydroxide by arsenious acid; and K. C. Sen, by sugar. S. G. Mokruskin and O. A. Esin examined the adsorption of aniline dyes by chromic oxide; N. Nikitin, the adsorption of ammonia; C. E. White and N. E. Gordon, and E. E. Porter, organic dyes; H. B. Weiser, oxalates; K. C. Sen, benzoic and acetic acids. They found that hydrated chromic oxide adsorbs acids and arsenious acid more than hydrated chromic or ferric oxides adsorbs arsenic trioxide; and N. R. Dhar and co-workers found that various metal salts—Zn, Cd, Co, and Ni—but not Ag salts, are adsorbed. According to E. Toporescu, when chromium is precipitated by ammonia from soln. of its salts containing calcium or magnesium, the amounts of these salts carried down increase with their concentration, and tend towards limits corresponding with the chromites, $Cr_2O_3.3CaO$ and $Cr_2O_3.3MgO$, respectively. The calcium or magnesium may be removed from such precipitates by washing them on the filter or by decantation with a boiling 5 per cent. soln. of ammonium nitrate. H. B. Weiser and E. E. Porter studied the effect of the $H^{\cdot}$-ion conc. of soln. on the adsorptivity of hydrated chromic oxide.

References.

[1] W. Ipatieff and A. Kisseleff, *Ber.*, **59**. B, 1418, 1826; *Journ. Russ. Phys. Chem. Soc.*, **58**. 664, 686, 692, 698, 1926; E. Guignet, *Rép. Chim. Pure*, **1**. 198, 1859; *Bull. Soc. Chim.*, (1), **3**. 76, 1861; C. Casthélaz and M. Leune, *Bull. Soc. Chim.*, (2), **10**. 170, 1868; J. Férée, *ib.*, (3), **25**. 620, 1901; S. Veil, *ib.*, (10), **5**. 135, 1926; *Compt. Rend.*, **182**. 1028, 1926; *Journ. Chim. Phys.*, **21**. 78, 1924; M. Poussier, *Ann. Chim. Phys.*, (2), **19**. 334, 1873; A. Scheurer-Kestner, *ib.*, (2), **3**. 26, 413, 1865; A. Recoura, *ib.*, (3), **6**. 909, 1891; *Ann. Chim. Phys.*, (6), **10**. 60, 1887; *Compt. Rend.*, **102**. 865, 1886; **120**. 1335, 1895; A. C. Becquerel, *ib.*, **67**. 1083, 1868; P. Bary and J. V. Rubio, *ib.*, **188**. 625, 1929; *Rev. Gén. Colloides*, **7**. 97, 1929; *Anal. Fis. Quim.*, **27**.

270, 1929; A. Salvétat, *Compt. Rend.*, **48**. 295, 1859; H. Baubigny, *ib.*, **98**. 103, 1884; F. Bourion and A. Sénéchal, *ib.*, **168**. 59, 89, 1919; E. M. Péligot, *ib.*, **21**. 24, 1845; L. Blanc, *Ann. Chim. Phys.*, (10), **6**. 182, 1926; L. Blanc and G. Chaudron, *Compt. Rend.*, **182**. 386, 1926; C. Meineke, *Liebig's Ann.*, **261**. 341, 1891; H. Schiff, *ib.*, **124**. 168, 1862; K. Seubert and A. Schmidt, *ib.*, **267**. 239, 1892; L. Schaffner, *ib.*, **51**. 169, 1844; A. Geuther, *ib.*, **118**. 66, 1861; G. Lösekann, *Ber.*, **12**. 57, 1879; R. F. Weinland and E. Guzzmann, *ib.*, **42**. 3881, 1909; E. Wedekind and W. Albrecht, *ib.*, **59**. B, 1726, 1926; W. Albrecht, *Magnetochemische Untersuchungen*, Elberfeld, 1927; G. F. C. Frick, *Pogg. Ann.*, **13**. 494, 1828; A. Schrötter, *ib.*, **53**. 513, 1841; M. Krüger, *ib.*, **61**. 218, 406, 1844; R. Bunsen, *ib.*, **91**. 619, 1854; M. Siewert, *Zeit. ges. Naturwiss.*, **18**. 244, 1861; O. T. Christensen, *Journ. prakt. Chem.*, (2), **23**. 26, 1881; J. Lefort, *Journ. Pharm. Chim.*, (3), **18**. 27, 1850; H. Löwel, *ib.*, (3), **7**. 321, 401, 424, 1845; E. Frémy, *Ann. Chim. Phys.*, (3), **23**. 388, 1847; *Compt. Rend.*, **47**. 884, 1858; E. Toporescu, *ib.*, **172**. 600, 1921; H. J. S. King, *Journ. Chem. Soc.*, **125**. 1329, 1924; **127**. 2100, 1925; J. M. Ordway, *Amer. Journ. Science*, (2), **26**. 202, 1858; H. Rinde, *Phil. Mag.*, (7), **1**. 32, 1926; M. Prud'homme, *Bull. Soc. Mulhouse*, **59**. 599, 1889; *Bull. Soc. Chim.*, (2), **17**. 253, 1872; G. Wyrouboff, *ib.*, (3), **27**. 666, 719, 1902; *Bull. Soc. Min.*, **24**. 86, 1901; N. A. Orlow, *Chem. Ztg.*, **31**. 1119, 1907; A. B. Northcote and A. H. Church, *Journ. Chem. Soc.*, **6**. 54, 1853; H. G. Denham, *ib.*, **93**. 41, 1908; C. F. Cross, *ib.*, **35**. 797, 1879; *Chem. News*, **44**. 209, 1879; A. J. W. Forster, *ib.*, **125**. 79, 1922; R. Kremann, *Zeit. anorg. Chem.*, **33**. 94, 1903; W. Herz, *ib.*, **28**. 344, 1901; **32**. 357, 1902; H. W. Fischer and W. Herz, *ib.*, **31**. 352, 1902; H. W. Fischer, *ib.*, **40**. 39, 1904; J. Olie, *ib.*, **52**. 62, 1906; R. Fricke, *ib.*, **166**. 244, 1927; **175**. 249, 1928; R. Fricke and F. Wever, *ib.*, **136**. 321, 1924; **172**. 304, 1928; O. Ruff and B. Hirsch, *ib.*, **146**. 388, 1925; N. Nikitin, *ib.*, **155**. 358, 1926; A. Hantzsch, *Zeit. anorg. Chem.*, **132**. 273, 1924; **30**. 338, 1902; R. Kremann, *ib.*, **33**. 87, 1903; E. Petersen, *Zeit. phys. Chem.*, **4**. 408, 1889; N. Bjerrum, *ib.*, **59**. 581, 1907; **73**. 724, 1910; **110**. 656, 1924; E. Müller, *ib.*, **110**. 363, 1924; R. Fricke and O. Windhausen, *ib.*, **113**. 248, 1924; *Zeit. anorg. Chem.*, **132**. 273, 1924; P. A. Thiessen and B. Kandelaky, *ib.*, **181**. 285, 1929; **182**. 425, 1929; F. Haber, *Naturwiss.*, **13**. 1007, 1925; *Ber.*, **55**. 1717, 1922; R. Schwarz, *ib.*, **57**. 1477, 1924; **58**. 73, 1925; A. Gutbier, J. Huber and W. Schieber, *ib.*, **55**. 1518, 1922; P. A. von Bonsdorff, *Pogg. Ann.*, **27**. 275, 1833; J. Bohm, *Zeit. anorg. Chem.*, **149**. 205, 1925; A. Simon and T. Schmidt, *ib.*, **153**. 191, 211, 1926; A. Simon and E. Thaler, *ib.*, **162**. 251, 1927; A. Simon, A. Fischer and T. Schmidt, *ib.*, **185**. 107, 1929; M. Berthelot, *Thermochimie*, Paris, **2**. 174, 1897; S. Veil, *Rev. Scient.*, **64**. 8, 1926; *Compt. Rend.*, **176**. 1304, 1923; A. Colson, *Ann. Chim. Phys.*, (8), **12**. 435, 457, 1907; V. Ipatieff and B. Mouromtseff, *Ber.*, **60**. B, 1980, 1927; J. J. Berzelius, *Schweigger's Journ.*, **22**. 60, 1318; L. Wöhler and W. Becker, *Zeit. angew. Chem.*, **21**. 1600, 1908; **24**. 484, 1911; L. Wöhler and J. Dierksen, *ib.*, **39**. 13, 1926; G. B. Frankforter, V. H. Rochrich, and E. C. Manuel, *Journ. Amer. Chem. Soc.*, **32**. 178, 1902; M. Neidle and J. Barab, *ib.*, **38**. 1961, 1916; H. N. Holmes and M. A. Dietrich, *ib.*, **48**. 678, 1926; J. Voisin, *Rev. Met.*, **7**. 1142, 1910; A. Eibner and O. Hue, *Farbenztg.*, **5**. 2106, 2157, 2213, 2268, 2319, 1910; C. Boniovanni, *Boll. Chim. Pharm.*, **49**. 789, 1910; J. M. van Bemmelen, *Die Absorption*, Dresden, 239, 1910; *Rec. Trav. Chim. Pays-Bas*, **7**. 37, 1888; J. R. I. Hepburn, *ib.*, **45**. 321, 1926; A. L. Baykoff, *Journ. Russ. Phys. Chem. Soc.*, **39**. 660, 1907; S. G. Mokruskin and O. A. Esin, *ib.*, **58**. 882, 1926; H. B. Weiser, *The Hydrous Oxides*, New York, 76, 1926; *Colloid Symposium Wisconsin*, 38, 1923; *Journ. Phys. Chem.*, **24**. 277, 505, 1920; **25**. 665, 1921; **26**. 409, 1922; **28**. 232, 428, 1253, 1924; **29**. 953, 1925; H. B. Weiser and E. E. Porter, *ib.*, **31**. 1383, 1704, 1824, 1927; H. B. Weiser and G. L. Mack, *ib.*, **34**. 86, 101, 1930; E. E. Porter, in H. B. Weiser, *The Hydrous Oxides*, New York, 91, 1920; S. Hakomori, *Journ. Japan. Chem. Soc.*, **43**. 629, 1922; J. H. Yoe and E. B. Freyer, *Journ. Phys. Chem.*, **30**. 1389, 1926; D. N. Chakravarti and N. R. Dhar, *ib.*, **30**. 1646, 1926; C. E. White and N. E. Gordon, *ib.*, **32**. 380, 1928; T. Graham, *Phil. Trans.*, **151**. 183, 1861; A. B. Dumansky, A. P. Buntin and A. G. Kniga, *Koll. Zeit.*, **41**. 108, 1927; A. Moberg, *Journ. prakt. Chem.*, (1), **29**. 175, 1843; M. Shipton in A. W. Hofmann, *Reports of Juries*, London, 75, 1863; J. B. Trommsdorff, *Trommsdorff's Journ.*, **18**. 223, 1829; R. Wintgen and W. Biltz, *Zeit. phys. Chem.*, **107**. 414, 1923; R. Wintgen and H. Weisbecker, *ib.*, **135**. 182, 1928; R. Wintgen and O. Kühn, *ib.*, **138**. 135, 1928; R. Wintgen and H. Löwenthal, *Koll. Zeit.*, **34**. 289, 296, 1924; *Zeit. phys. Chem.*, **109**. 378, 1924; W. Biltz, *Ber.*, **35**. 4431, 1902; **37**. 1095, 1904; W. Biltz, K. Meisel and G. A. Lehrer, *Zeit. anorg. Chem.*, **172**, 304, 1928; W. Biltz and W. Geibel, *Gött. Nachr.*, 144, 1906; C. Paal, *ib*,. **47**. 2211, 1914; A. Miolati and E. Mascetti, *Gazz. Chim. Ital.*, **31**. i, 93, 1901; *Atti Accad. Lincei*, (5), **14**. i, 217, 1905; J. K. Wood and V. K. Black, *Journ. Chem. Soc.*, **109**. 164, 1916; H. W. Woudstra, *Koll. Zeit.*, **5**. 33, 1909; *Chem. Weekbl.*, **6**. 375, 1909; C. F. Nagel, *Journ. Phys. Chem.*, **19**. 331, 569, 1915; E. H. Bunce and L. S. Finch, *ib.*, **19**. 331, 1914; H. M. Goodwin and F. W. Grover, *Phys. Rev.*, (1), **11**. 193, 1900; W. D. Bancroft, *Applied Colloidal Chemistry*, New York, 244, 1921; *Trans. Amer. Electrochem. Soc.*, **28**. 351, 1915; *Chem. News*, **113**. 113, 1916; S. Prakash and N. R. Dhar, *Journ. Phys. Chem.*, **34**. 954, 1930; *Journ. Indian Chem. Soc.*, **6**. 491, 1929; **7**. 591, 1930; W. V. Bhagwat and N. R. Dhar, *ib.*, **6**. 781, 1929; K. C. Sen, *Journ. Phys. Chem.*, **31**. 922, 1840, 1927; *Biochem. Zeit.*, **169**. 192, 1926; *Koll. Zeit.*, **36**. 193, 1925; **43**. 17, 1927; *Zeit. anorg. Chem.*, **182**. 129, 1929; *Journ. Indian Chem. Soc.*, **4**. 131, 1927; N. R. Dhar and V. Gore, *ib.*, **6**. 31, 1929; S. Ghosh and N. R. Dhar, *ib.*, **5**. 303, 1928; **6** 31, 1929; K. Mohanlal and N. R. Dhar, *Zeit. anorg. Chem.*, **174**. 1, 1928; K. C. Sen, *ib.*, **174**. 61, 75, 1928; **182**. 118, 129, 1929; S. Roy and N. R. Dhar, *Journ. Phys. Chem.*, **34**. 122, 1930; N. G. Chatterji and

N. R. Dhar, *Chem. News*, **121**. 253, 1920 ; K. C. Sen and N. R. Dhar, *Koll. Zeit.*, **34**. 262, 1924 ; K. C. Sen and M. R. Mehrotra, *Zeit. anorg. Chem.*, **142**. 345, 1925 ; *Koll. Zeit.*, **42**. 35, 1927 ; S. L. Jindal and N. R. Dhar, *Chem. News*, **133**. 177, 1926 ; N. R. Dhar, K. C. Sen and N. G. Chatterji, *Zeit. Koll.*, **33**. 29, 1923 ; S. Ghosh and N. R. Dhar, *ib.*, **41**. 289, 1927 ; *Journ. Indian Chem. Soc.*, **4**. 173, 1927 ; *Journ. Phys. Chem.*, **29**. 435, 1925 ; **30**. 622, 830, 1926 ; *Zeit. anorg. Chem.*, **152**. 404, 1926 ; B. Reinitzer, *Monatsh.*, **3**. 249, 1882 ; M. Z. Jovitschitsch, *ib.*, **34**. 225, 1913 ; *Helvetica Chim. Acta*, **3**. 46, 1920 ; *Compt. Rend.*, **158**. 872, 1914 ; J. Häusler and B. Kohnstein, *Austrian Pat. No.* 106829, 1921 ; M. Kreps, *Ueber salzartige Verbindungen des Chromoxyds mit Alkalien und Erden*, Berlin, 1926 ; A. Ivanitzkaja and L. Orlova, *Koll. Beihefte*, **18**. 1, 1923 ; A. Lottermoser, *Zeit. Elektrochem.*, **30**. 391, 1924 ; W. Herz, *Jahresb. Schlesis. Ges. Vaterländ Kultur.*, **82**. ii, 144, 1904 ; W. Reinders, *Chem. Weekbl.*, **23**. 130, 1926 ; H. Gordon, *Ueber die Komplexität verschiedener Metalltartrationen und die Löslichkeit verschiedener Metallhydroxyde und Sulfide*, Danzig, 1924 ; K. Jellinek and H. Gordon, *Zeit. phys. Chem.*, **112**. 207, 1924 ; W. Pauli and E. Valko, *Zeit. phys. Chem.*, **121**. 161, 1926 ; P. Hausknecht, *Magnetochemische Untersuchungen*, Strassburg, 1913 ; R. Fricke, C. Gottfried, W. Skaliks, A. Munchmeyer and F. Engelhardt, *Zeit. anorg. Chem.*, **166**. 244, 1927 ; L. Havestadt and R. Fricke, *ib.*, **188**. 357, 1930 ; B. Kandelaky, *Chromiäthylat : Darstellung und Hydrolyse*, Göttingen, 1929 ; R. Griessbach and J. Eisele, *U.S. Pat. No.* 1775640, 1930 ; V. Ipatéeff, *Ber.*, **63**. B, 2365, 1930 ; L. Havestadt and R. Fricke, *Zeit. anorg. Chem.*, **188**. 357, 1930 ; H. R. Robinson and C. L. Young, *Phil. Mag.*, (7), **10**. 71, 1930 ; T. Ishiwara, *Science Rep. Tohoku Univ.*, **3**. 303, 1914 ; T. Katsurai, *Science Papers Japan. Inst. Phys. Chem. Research*, **12**. 161, 1929 ; E. Manegold and R. Hofmann, *Koll. Zeit.*, **51**. 220, 1930 ; **52**. 201, 1930 ; A. Lottermoser and W. Riedel, *ib.*, **51**. 30, 1930 ; **52**. 133, 1930 ; S. Horiba and H. Baba, *Journ. Phys. Chem. Japan*, **3**. 1, 1929 ; S. Takegami, *Bull. Japan. Chem. Soc.*, **4**. 156, 1929.

§ 11. Chromites

Hydrated chromic oxide shows pronounced basic properties uniting with acids to form tervalent chromium salts. It is, however, an amphoteric oxide and it acts as a weak base forming salts—**chromites**—which have the spinel formula $RO.Cr_2O_3$, or $R(CrO_2)_2$. These salts can be regarded as **metachromites** derived from **metachromous acid,** $HCrO_2$, or $HO.CrO$; there are also indications of the formation of **orthochromites,** derived from **orthochromous acid,** H_3CrO_3, or $Cr(OH)_3$. According to F. Hein and H. Meininger,[1] chromium triphenylhydroxide $Cr(C_6H_5)_3OH$ is nearly as strong a base as sodium hydroxide. R. Wintgen and H. Weisbecker studied the amphoteric properties of chromic oxide hydrosol.

Z. Weyberg reported crystals of **lithium chromite,** $LiCrO_2$, to be formed along with lithium aluminate when mixtures of an excess of lithium chromate with china clay are calcined. The brown powder consists of microscopic, isotropic, octahedral crystals. As previously indicated, there are differences of opinion as to the nature of the green liquid obtained when freshly precipitated hydrated chromic oxide is treated with alkali-lye. The process is one of either peptization or dissolution ; or else it includes both. R. Kremann, M. Kreps, and J. K. Wood and V. K. Black consider that the soln. of hydrated chromic oxide in alkali is chromite ; while W. Herz and H. W. Fischer, A. Hantzsch, C. F. Nagel, W. V. Bhagwat and N. R. Dhar, and H. B. Weiser consider it to be peptized, hydrated chromic oxide. C. Fricke and O. Windhausen determined the solubility of hydrated chromic oxide approximating $Cr_2O_3.9H_2O$, expressed in grms. Cr_2O_3 per 100 c.c. of soln., after three days' digestion in a soln. of sodium hydroxide at ordinary temp. and obtained the following results :

N-NaOH .	0·5	0·71	5·10	9·89	10·00	11·06	14·15	15·63
Cr_2O_3 .	0·25	0·5	1·58	2·89	2·68	1·90	0·80	0·40
K or K' .	3·6	3·4	3·2	3·4	2·7	2·6	2·3	1·5
	$NaCrO_2$				Na_3CrO_3			

With $17·42N$-NaOH, the soln. was almost colourless, $K=[NaOH]/[Cr]$, and $K'=[NaOH]^3/[Cr]$. The results are plotted in Fig. 20.

According to E. Müller, the equilibrium condition between a soln. of sodium hydroxide and chromic hydroxide is very slowly attained. The curves, Fig. 21, rise to a maximum and then fall to a minimum value, due, it is supposed, to the chromic hydroxide dissolving unchanged in the lye ; it then changes by the loss of water into a less soluble oxide, a change which is accelerated by heat. It is assumed that the equilibrium conditions are: $Cr(OH)_3 + 3NaOH \rightleftharpoons Na_3CrO_3 + 3H_2O$; $Cr(OH)_3 + 2NaOH \rightleftharpoons Na_2HCrO_3 + 2H_2O$; and $Cr(OH)_3 + NaOH \rightleftharpoons NaH_2CrO_3 + H_2O$; followed by $NaH_2CrO_3 + H_2O \rightleftharpoons NaCrO_2 + 2H_2O$. R. Fricke and O. Windhausen studied this subject and found that when hydrated chromic oxide is treated with sodium hydroxide, the formation of chromite precedes the formation of the hydroxide. With sodium hydroxide below 10*N*, primary sodium chromite is formed, whilst above 10*N* the soln. contains also tertiary sodium chromite. Potassium chromite is similarly produced; below 8*N*-alkali only the primary chromite is formed, whilst above 8*N* the soln. contains also secondary chromite. From soln. of potassium chromite which have stood for a long time, needle-shaped crystals of the formula $Cr_2O_3.3K_2O.8H_2O$ have been obtained. R. B. Corey found that the clear supernatant liquor left by chromic hydroxide settling from soda-lye contains no chromium, showing that chromic hydroxide is insoluble in that menstruum, and the apparent solubility is really peptization and not a case of soln. N. Demassieux and J. Heyrovsky inferred that soln. of alkali chromite are not true soln. but contain colloidal chromic hydroxide. The primary **sodium metachromite,** $NaCrO_2$, is formed with alkali-lye below 10*N*-NaOH; and **sodium orthochromite,** Na_3CrO_3, above that conc. J. d'Ans and J. Löffler obtained $NaCrO_2$ by the action of chromic oxide on sodium hydroxide. J. Heyrovsky obtained similar results with potassium hydroxide as those obtained with soln. of sodium hydroxide; below 8*N*-KOH, only **potassium metachromite,** $KCrO_2$, is formed, and above that concentration, **potassium orthochromite,** K_3CrO_3. Z. Weyberg found that by melting mixtures of china clay and alkali chromate, chromic oxide first separates out, and afterwards the chromite. If the soln. of potassium chromite be allowed to stand for a long time, needle-shaped crystals of the tetrahydrate, $K_3CrO_3.4H_2O$, are deposited. These conclusions were confirmed by observations on the f.p., and potential of the soln. M. Kreps could not prepare potassium and sodium chromites in the dry way, because in subsequently washing out the excess of alkali with water, the chromite is decomposed. R. Kremann found that the movements towards the anode of the green soln. of hydrated chromic oxide in conc. alkali-lye demonstrates the existence of chromites; the hydrated chromic hydroxide is not present merely as a colloid because it can diffuse through parchment into the alkaline soln. H. P. Cady and R. Taft found potassium chromite to be insoluble in liquid sulphur dioxide. P. C. Boudault said that potassium ferricyanide oxidizes a soln. of potassium chromite to chromate. The salt is sparingly soluble in acids.

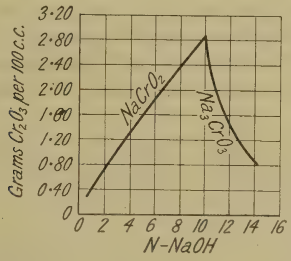


FIG. 20.—The Solubility of Hydrated Chromic Oxide in Solutions of Sodium Hydroxide.

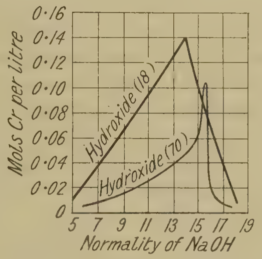


FIG. 21.—The Solubility of Chromic Hydroxide in Solutions of Sodium Hydroxide.

J. F. Persoz obtained **cuprous chromite,** $CuCrO_2$, by calcining cupric chromate in a crucible exposed to the reducing action of the furnace gases, and extracting the product with hydrochloric acid; and L. and P. Wöhler obtained it by heating one of the basic cupric chromites with an excess of cupric oxide above 900°, and extracting the mass with nitric acid of sp. gr. 1·4. Cuprous chromite forms steel-blue or lead-grey triangular plates of sp. gr. 5·237. It is stable in oxygen above 875°, and in air above 770°. It does not oxidize in oxygen at a press. of 1087 mm. at 1020°. It is soluble in nitric acid of sp. gr. 1·4; but a mixture of nitric acid and potassium chlorate oxidizes the chromium to chromic acid. K. Fischbeck and E. Einecke prepared this salt and found that by cathodic polarization in 2 per cent. sulphuric acid, it is oxidized to chromate. L. and P. Wöhler and W. Plüddemann tried the salt as a catalytic agent for oxidizing sulphur dioxide.

J. F. Persoz obtained **cupric chromite,** $Cu(CrO_2)_2$, by heating to redness cupric chromate—L. and P. Wöhler worked above 870°—and extracting the product with hydrochloric acid; L. and P. Wöhler obtained it by heating the cuprous salt in oxygen below 870°, and extracting the mass with nitric acid; they precipitated mixed cupric and chromic hydroxides from a soln. of the mixed sulphates in eq. proportions by means of sodium carbonate, heated the washed product in oxygen at 700°, and then extracted it with dil. acids; C. H. Boehringer treated a soln. of basic cupric chloride with copper tetramminoxide; and M. Gerber heated to redness a mixture of cupric chloride and potassium dichromate, and washed the product first with boiling water, and then with hydrochloric acid. The bluish-black amorphous or crystalline product decomposes slowly at 1000°. If the compound be mixed with cupric oxide, and heated in vacuo, oxygen begins to be given off at 600°. The partial press. of the oxygen is 176 mm. at 779°; 440 mm. at 840°; and 795 mm. at 875°. At 850°, 38 Cals. are needed. The salt is not soluble in dil. acids, or in conc. hydrochloric acid; it is not attacked by sulphur dioxide; but it is oxidized by fused potassium nitrate. F. Wöhler and F. Mahla, and L. and P. Wöhler and W. Plüddemann studied its action as a catalyst in the oxidation of sulphur dioxide.

L. and P. Wöhler and co-workers obtained a basic salt, *cupric oxyoctochromite*, $CuO.4Cu(CrO_2)_2$, by heating commercial cupric chromate, in oxygen at 650°–700°, and extracting the mass with nitric acid. The black product decomposes at 1000°. M. Rosenfeld obtained *cupric trioxychromite*, $3CuO.Cu(CrO_2)_2$, by heating $6CuO.Cr_2O_3.CrO_3$; *cupric hexoxychromite*, $6CuO.Cu(CrO_2)_2$, by heating $7CuO.2CrO_3.5H_2O$; and *cupric tridecoxychromite*, $13CuO.Cu(CrO_2)_2$, by heating $7CuO.CrO_3.5H_2O$; and the acid salt, *cupric hexachromite*, $CuO.3Cr_2O_3$, by heating $CuCr_4O_9.Cr_2O_3.12H_2O$.

According to K. S. Nargund and H. E. Watson, mixtures of calcium and chromic oxides, when heated in vacuo, yield **calcium chromite,** $Ca(CrO_2)_2$; which when treated with acids, yields $CaO.2Cr_2O_3$. Z. Weyberg obtained the same product as prismatic, pleochroic, green needles by melting china clay with a large excess of potassium chromate and calcium oxide. M. Kreps obtained calcium chromite by adding ammonia to mixed soln. of calcium chloride and chrome-alum. F. de Carli said that the reaction between chromic oxide and calcium oxide begins at 550°. M. Gerber prepared calcium chromite by melting a mixture of mol. proportions of potassium dichromate and anhydrous calcium chloride, extracting the mass with water, and washing the product with boiling, conc. hydrochloric acid. E. Dufau obtained it by heating a mixture of chromic and calcium oxides in an electric furnace. K. Fischbeck and E. Einecke prepared this salt by direct sintering of the components. E. Dufau found that the dark olive-green product furnishes a crystalline powder, or pleochroic, prismatic needles, and it has a sp. gr. of 4·8 at 18°, and a hardness of 6. When heated in oxygen, it forms calcium chromate and chromic oxide; the oxidation begins below 100° in air; it is attacked by fluorine, or chlorine when warmed; hydrogen fluoride or chloride attacks it at a red-heat, but hydrofluoric or hydrochloric acid has no action, nor has sulphuric or nitric acid. It is decomposed by molten potassium carbonate, nitrate, or chlorate; Z. Weyberg added that it is slowly attacked by potassium hydrosulphate. T. J. Pelouze prepared **calcium oxychromite,** $CaO.Ca(CrO_2)_2$, by adding potassium hydroxide or ammonia to a mixture of a mol of chrome-alum and 2 mols of calcium chloride; H. Moissan obtained **calcium trioxychromite,** $3CaO.Ca(CrO_2)_2$, in yellow plates, by heating chromium and calcium oxide in an electric furnace ; and E. Dufau, by heating a mixture of chromic and calcium oxides in the electric furnace. It might be added that the pottery colour, emerald green, is prepared by heating chromic oxide with a large proportion of calcium carbonate. A. Mitscherlich obtained **barium chromite,** $Ba(CrO_2)_2$, by heating a mixture of chromic and barium oxides to a white-heat. The crystals are soluble in hydrochloric acid ; and M. Gerber obtained it as a green crystalline powder by melting a mixture of anhydrous barium chloride and potassium dichromate, and washing the cold product with dil. hydrochloric acid. M. Kreps also prepared barium chromite by the action of ammonia on a soln. of chrome-alum and barium chloride. F. de Carli said that the reaction with chromic oxide and barium oxide begins at 220°. E. Dufau obtained **barium octochromite,** $BaO.4Cr_2O_3$, in black, hexagonal crystals of sp. gr. 5·4 at 15°, by heating a mixture of the two oxides in an electric arc-furnace. The product is stable. When heated in oxygen, it forms barium chromate and chromic oxide ; it is slowly attacked when heated with hydrogen fluoride or chloride ; acids are without action ; but it is easily attacked by fused alkali carbonate.

E. Mallard and J. J. Ebelmen melted together beryllium and chromic oxides in the presence of boric oxide, and obtained a dark green powder consisting of crystals of **beryllium chromite,** $Be(CrO_2)_2$. The crystals resemble alexandrite. The so-called *chrome spinel,* $(Mg,Fe)O.(Al,Cr)_2O_3$, from Lherz was called *lherzolite* by J. C. Delamétherie, but it was described earlier by P. Picot de la Peyrouse, and hence the name *picotite.* G. M. Bock, M. Websky, and A. Breithaupt described a related mineral which was called *magnochromite,* or *magnesiochromite—vide infra,* chromite. Analyses of picotite and magnesiochromite were reported by T. Thomson, B. Kosmann, F. Sandberger, A. Damour, A. Hilger, G. C. Hoffmann, C. Friedheim, and T. Petersen. E. S. Simpson proposed the term **picrochromite** —πικρός, bitter, in allusion to the bitter taste of magnesium salts—for members of the spinel-chromite series approaching in composition $Mg(CrO_2)_2$, discussed by T. S. Hunt, T. Petersen, E. Glasser, etc. There are four components, and the end-terms are: (1) *spinel,* $Mg(AlO_2)_2$—including spinel, ceylonite, and magnesiochromite ; (2) *hercynite,* $Fe(AlO_2)_2$—including hercynite and picotite ; (3) *picrochromite,* $Mg(CrO_2)_2$—including picrochromite and chromopicotite or magnesiochromite ; and (4) *chromite,* $Fe(CrO_2)_2$—including chromite, and beresofite. J. J. Ebelmen obtained **magnesium chromite,** $Mg(CrO_2)_2$, by melting a mixture of chromic and magnesium oxide with boric oxide in a porcelain oven, and extracting the product with hydrochloric acid. E. Schweitzer obtained it by calcining potassium magnesium chromate and extracting the residue with dil. and afterwards with hot conc. acid ; K. Fischbeck and E. Einecke, by the sintering of the components ; M. Gerber, by melting a mixture of anhydrous magnesium chloride and potassium dichromate, and extracting the product with hot conc. hydrochloric acid ; W. R. Nichols, by adding an excess of ammonia to a soln. of a mixture of a mol of magnesium sulphate and 1·19 mols of chrome-alum and some ammonium chloride—M. Kreps used a similar process—and E. Dufau, by heating in the electric arc-furnace a mixture of chromic and magnesium oxides. M. L. Huggins showed that the crystals are of the spinel type, and he discussed the electronic structure. S. Holgersson found that the X-radiogram gave for the lattice parameter $a=8{\cdot}32$ A. and the sp. gr. 4·45 ; L. Passerini gave $a=8{\cdot}29$ A., the sp. gr. 4·49, and the vol. of unit cell $569{\cdot}72\times10^{-24}$ c.c. J. J. Ebelmen said that the dark green octahedra have a sp. gr. 4·415 at 15° and scratch glass but not quartz. E. Dufau gave 4·6 for the sp. gr. at 20°, and said that the hardness is greater than that of quartz. F. Beijerinck found that it is a good conductor of electricity ; but it is not magnetic. E. Dufau observed that the compound is not changed when strongly heated ; it is oxidized with difficulty by oxygen at a red-heat ; it is not attacked by chlorine or bromine ; it is attacked with difficulty by hydrofluoric or hydrochloric acid ; J. J. Ebelmen said that it is not attacked by conc. hydrochloric acid. E. Dufau, and E. Schweitzer found that it is easily attacked by hot, conc. sulphuric acid ; it is not attacked by boiling nitric acid; it is insoluble in alkali-lye; and it is slowly attacked by molten potassium nitrate and chlorate—and, added W. R. Nichols, it is slowly oxidized to chromate by fused sodium carbonate and potassium nitrate. W. R. Nichols obtained **magnesium oxychromite,** $MgO.Mg(CrO_2)_2$, by adding an excess of ammonia to a mixed soln. of chrome-alum and an excess of magnesium sulphate. G. Viard obtained it as a pale brown powder, by calcining at a red-heat either magnesium chromate, or potassium magnesium chromate. When further heated it passes into **magnesium oxyoctochromite,** $MgO.4Mg(CrO_2)_2$; if potassium dichromate mixed with magnesium oxide be heated to redness, **magnesium oxytetrachromite,** $MgO.2Mg(CrO_2)_2$, is formed. According to M. R. Nayar and co-workers, magnesium chromate decomposes at 650°, forming chromites from which the magnesium oxyoctochromite, $MgO.4Mg(CrO_2)_2$, can be obtained as an insoluble residue after extraction with hydrochloric acid; a mixture of equimolar proportions of magnesia and chromic oxide above 600° yields **magnesium oxydecachromite,** $MgO.5Mg(CrO_2)_2$. W. R. Nichols prepared **magnesium tetrachromite,** $MgO.2Cr_2O_3$, by adding ammonia to a mixed soln. of a mol of magnesium sulphate and 2·02 mols of chrome-alum.

J. J. Ebelmen prepared **zinc chromite,** $Zn(CrO_2)_2$, by the method used for the magnesium salt; M. Gerber, by heating a mixture of anhydrous zinc chloride and an excess of potassium dichromate; G. Chancel, and M. Gröger, by adding potassium hydroxide to a mixed soln. of equimolar parts of a zinc and a chromic salt; and G. Viard, by passing the vapour of zinc chloride in a current of nitrogen or carbon dioxide over heated potassium chromate, and washing the mass with water, and conc. hydrochloric acid. K. Fischbeck and E. Einecke made it as in the case of the magnesium salt. M. L. Huggins showed that the crystals are of the spinel type and he discussed the electronic structure. According to J. J. Ebelmen, the black octahedral crystals have a sp. gr. 5·309, and they are harder than quartz. G. Viard gave 5·29 for the sp. gr. at 13°. L. Passerini calculated 4·436 for the sp. gr. from the lattice data; and found the lattice has the side a=8·280 A.; S. Holgersson gave a=8·323 A. W. Biltz and co-workers discussed the mol. vol. E. W. Flosdorf and G. B. Kistiakowsky examined a mixture of chromic and zinc oxides as a catalyst.

M. Gröger prepared violet-brown *zinc pentoxyhexachromite,* $5ZnO.3Zn(CrO_2)_2$, by heating potassium zinc chromate, and extracting the product with water; G. Viard obtained *zinc oxydichromite,* $ZnO.Zn(CrO_2)_2$, by calcining ammonium zinc chromate; *zinc oxytetrachromite,* $ZnO.2Zn(CrO_2)_2$, by calcining a mixture of zinc chloride and potassium chromate; and *zinc oxydecachromite,* $ZnO.5Zn(CrO_2)_2$, by calcining at a red-heat a mixture of zinc oxide and potassium dichromate.

G. Viard obtained **cadmium chromite,** by passing the vapour of cadmium chloride, in a current of nitrogen or carbon dioxide, over potassium chromate at a white-heat; also by heating cadmium chromate to dull redness, or likewise by heating a mixture of cadmium oxide and potassium dichromate. K. Fischbeck and E. Einecke made it as in the case of the magnesium salt. M. L. Huggins showed that the crystals are of the spinel type and he discussed the electronic structure. S. Holgersson gave a=8·60 A. for the lattice parameter, and 5·84 for the sp. gr. According to G. Viard, the black, octahedral crystals have a sp. gr. of 5·79 at 17°; they scratch glass but not quartz; and they are stable in acids.

L. Passerini found that chromic oxide forms a series of solid soln. when it is heated with alumina, but no **aluminium chromite** is formed; the lattice constants of the solid soln. range from a=4·950 A. for Cr_2O_3 to 4·740 A. for Al_2O_3, and c=6·806 A. to 6·478 A. S. Veil heated compressed mixtures of ceric and chromic oxides, and determined the electrical conductivities and coeff. of magnetization of the mixtures. The resulting curves indicated the existence of **ceric dichromite,** $CeO_2.Cr_2O_3$; **ceric tritoctochromite,** $3CeO_2.4Cr_2O_3$; **ceric tetrachromite,** $CeO_2.2Cr_2O_3$, or $Ce(CrO_2)_4$; and **ceric decachromite,** $CeO_2.5Cr_2O_3$; and the probable existence of **ceric pentitadichromite,** $5CeO_2.Cr_2O_3$; **ceric heptitoctochromite,** $7CeO_2.4Cr_2O_3$; and

ceric octodecachromite, $CeO_2.9Cr_2O_3$. G. Chancel mixed alkaline soln. of lead and chromic oxides, and obtained a green precipitate of **lead chromite,** $Pb(CrO_2)_2$. S. H. C. Briggs obtained **antimony oxychromite,** $2Sb_2O_3.Cr_2O_3$, by heating 3·5 grms. of antimony oxychloride, $2SbOCl.Sb_2O_3$, with 8 grms. of chromic trioxide and 8 c.c. of water in a sealed tube for 5 hrs. at 200°. The brown powder was thoroughly washed and dried. It was insoluble in alkali-lye, water, acids, and aqua regia. S. H. C. Briggs heated a mixture of 5 grms. of bismuth oxychloride, 6 grms. chromic trioxide, and 6 c.c. of water in a sealed tube at 200° for 5 hrs. The brown product, **bismuth oxychromite,** $3Bi_2O_3.2Cr_2O_3$, resembled antimony oxychromite. For **tungstic chromite,** *vide infra,* chromium tungstate. C. F. Rammelsberg obtained what was thought to be a yellowish-brown precipitate of **uranium chromite** mixed with chromate by treating uranium tetrachloride with potassium chromate.

J. J. Ebelmen obtained **manganese chromite,** $Mn(CrO_2)_2$ by heating a mixture of manganous and chromic oxides and boric oxide in a porcelain oven, and washing the product with hot, conc. hydrochloric acid. K. Fischbeck and E. Einecke made it as in the case of the magnesium salt. M. Gerber obtained it by melting a mixture of anhydrous manganese chloride and potassium dichromate. M. L. Huggins showed that the crystals are of the spinel type and he discussed the electronic structure. J. J. Ebelmen found that the iron-grey, octahedral crystals have a sp. gr. of 3·87. S. Holgersson gave for the space-lattice a=8·487 A. J. J. Ebelmen found that the crystals scratch glass ; they resist attack by acids, and are oxidized by molten potassium hydroxide and potassium nitrate—*vide infra,* manganese chromate.

The discovery of **ferrous chromite,** $Fe(CrO_2)_2$, or $FeO.Cr_2O_3$, by L. N. Vauquelin[2] has been previously discussed. The occurrence and some analyses of the mineral have also been indicated.

Analyses have been reported by H. Abich, E. Bechi, E. Berthier, G. M. Bock, J. C. Booth and C. Lea, L. H. Borgström, A. Christomanos, F. W. Clarke, E. Divers, L. Duparc and S. P. de Rubies, T. H. Garrett, A. Hilger, A. Hofmann, G. C. Hofmann, K. von John and C. F. Eichleitner, M. Z. Jovicic, E. Kaiser, A. Knop, F. Kovar, H. E. Kramm, A. Lacroix, A. Laugier, A. Liversidge, W. G. Maynard, G. P. Merrill, A. Moberg, H. Pemberton, T. Petersen, J. H. Pratt, G. T. Prior, C. F. Rammelsberg, L. E. Rivot, F. Ryba, H. Seybert, E. V. Shannon, E. S. Simpson, J. L. Smith, W. Tassin, H. Traube, G. Tschermak, F. W. Voit, T. Wada, W. Wallace and R. M. Clark, M. Websky, and A. E. V. Zeally.

The formula was discussed by C. F. Rammelsberg, P. Niggli, E. S. Simpson, N. Federowsky, and A. Lacroix. L. W. Fisher found that pure chromite has been found only in meteorites ; with other varieties there is a wide variation in the proportions of acid and base. Nearly all the chromites which have been analyzed show one or more oxides in excess. This may be due to incomplete separation of chromite and gangue. Consequently, its composition can seldom be represented by a definite formula. Chromite is a member of the spinel family, but all the family cannot be represented in definite isomorphous series.

The mineral was called *iron-chrome,* or rather *Eisenchrom* by P. Meder, and D. L. G. Karsten ; *siderchrom,* by J. J. N. Huot ; *chromoferrite,* by E. J. Chapman ; and **chromite,** by W. Haidinger. Although the composition approximates $Fe(CrO_2)_2$, the iron may be in part replaced by magnesium to form *magnochromite* or *magnesiochromite* (*q.v.*), specimens of which were described by A. Breithaupt, M. Websky, and G. M. Bock. Some of the chromium may be replaced by aluminium and by ferric iron as in the *chromopicotite* from the Dun Mt., New Zealand, described by T. Petersen. Chromite thus merges by gradations into spinel—*e.g. picotite.* A. Lacroix described a black mineral from Madagascar to which he gave the name *chromohercynite,* and its composition approximated $Fe(CrO_2)_2.(Fe,Mg,Mn)(AlO_2)_2$, and its sp. gr. 4·415. According to H. Arsandaux, the chromite of Mow Djeti, Togo, is a *chromiferous ferropicotite,* $(Mg,Fe,Mn)O.(Cr,Al,Fe)_2O_3$. The *mitchellite* of J. H. Pratt can be represented by $(Fe,Mg)O.(Cr,Al)_2O_3$. The mineral *chromitite* obtained by M. Z. Jovicic from Western Siberia is possibly a mixture of chromite and magnetite. The incomplete analysis corresponds with $Fe_2O_3.Cr_2O_3$, but ferric and ferrous oxides are not distinguished in the analysis. The sp. gr. is 3·1. H. Forestier and G. Chaudron found that ferric and chromic oxides form solid soln.

The special occurrence of chromite was discussed by A. Arzruni, E. Berwerth, E. Cohen and E. Weinschenk, L. Colomba, J. S. Diller, C. Doelter, E. von Federoff and W. Nikitin, L. Cascuel, A. C. Gill, S. G. Gordon, H. S. Harger, R. Helmhacker, V. Hilber and I. Ippen, F. C. Hochstetter, C. Hütter, E. Kaiser, P. Kato, J. H. Lewis, A. Liversidge, L. F. Lubogetzky, R. W. E. MacIvor, H. B. Maufe and co-workers, M. P. Melnikoff, A. Michel-Lévy, J. H. Pratt, A. Rocati, B. Simmersbach, E. V. Shannon, A. Stella, O. Stutzer, P. A. Wagner, W. Wallace and R. M. Clark, O. Weiss, H. E. Williams, F. Zirkel, etc.—*vide supra*, the occurrence of chromium.

The origin of chromite was discussed by B. Baumgärtel, F. Beyschlag and co-workers, C. Camsell, A. Himmelbauer, A. de Launay, J. H. Pratt, F. Ryba, G. M. Schwartz, E. Sampson, L. W. Fisher, F. E. Keep, C. S. Ross, J. T. Singewald, J. H. L. Vogt, and P. A. Wagner. The occurrence of chromite in meteorites was described by E. Cohen, A. Daubrée, A. Eberhard, L. Fletcher, H. B von Foullon, W. Haidinger, O. W. Huntington, G. F. Kunz, A. Laugier, N. S. Maskelyne, C. F. Rammelsberg, G. Rose, C. U. Shepard, J. L. Smith, F. Stromeyer, G. Tschermak, T. N. Tschernyschoff, R. D. M. Veerbeck, V. Wartha, and F. Wöhler.

J. J. Ebelmen obtained black octahedral crystals by heating in a porcelain oven a mixture of chromic and ferric oxides, tartaric acid, and boric oxide; S. Meunier, by heating a mixture of iron filings, ferrous carbonate and potassium dichromate, or a mixture of alumina, colcothar, chromic oxide, and cryolite, or a mixture of chrome oxide, ferrous chloride, in a crucible lined with cryolite; and M. Gerber, by melting a mixture of anhydrous ferrous chloride and potassium dichromate. Chromite was also prepared by J. A. Hedvall, and K. Fischbeck and E. Einecke, by heating an intimate mixture of the component oxides; and by S. Meunier, by heating chlorides of iron and chromium in hydrogen, and afterwards in steam. J. H. Pratt found a peridotitic magma, containing an excess of magnesia, and a little aluminium and chromic oxides, in which crystals of chromite were present; and J. H. L. Vogt observed that chromite and picotite seem to separate first from such magmas. J. Clouet, and F. Fouqué and A. Michel-Lévy described crystals of a product with crystals like those of chromite, but with the composition **ferrous oxychromite,** $FeO.Fe(CrO_2)_2$; they were obtained by adding ammonia to a mixed soln. of iron and chromium sulphates, and heating the precipitate with borax. C. Sandonnini observed that no ferrite is formed when a mixture of ferrous and chromic hydroxides is oxidized.

Chromite commonly occurs in granular or compact masses of an iron-black or brownish-black colour, which, according to J. Thoulet, may be yellowish- or brownish-red when viewed by transmitted light in thin sections. Chromite also occurs in octahedral crystals described by E. Hussak. J. Königsberger proved that the crystals are isotropic. G. Sukkow found some crystals twinned according to the spinel law; and A. Knop observed some chromite crystals with growths of rutile and zircon. Ferrous and magnesium chromites form solid soln.; so also do ferrous chromite and ferrous aluminate. There is also evidence that some ferrites and chromites form solid soln. L. W. Fisher found that members of the spinel family are not always isomorphous, but that these series are so: (i) spinel, magnochromite, and chromite; (ii) magnetite, kreittonite, dysluite, and jahrite; (iii) spinel, magnesioferrite, and magnetite; and (iv) gahnite, spinel, and franklinite. P. F. Kerr studied the X-radiograms; and P. E. Wretblad, and L. Passerini found that ferric and chromic oxides furnish a complete series of solid soln. with cells having axial ratios and densities which are linear functions of the composition. The subject was discussed by G. Grenet. L. Tokody found that the cubic lattice of chromite has a=8·05 A., and eight mols. per unit lattice; and S. Holgersson gave

a=8·319 A. P. Niggli discussed the lattice structure which is taken to be that of the spinels—*vide* magnetite. H. Schneiderhöhn discussed the microstructure of polished sections of the mineral. L. W. Fisher said that the colour of these sections corresponds roughly with the chemical composition. With a low proportion of chromic oxide as in picotite, the colour is yellowish-brown; and with a high proportion of chromic oxide the colour is deep cherry-red or coffee-brown. Anastomosing black, opaque lines traversing translucent grains are due to the presence of a foreign substance present either as a solid soln., or deposited as a cement along narrow or incipient fractures. The sp. gr. of the mineral ranges from 4·1 to 4·9; E. F. Harroun and E. Wilson gave 3·88 to 4·15. J. J. Ebelmen's artificial chromite had a sp. gr. of 4·97—*vide infra.* The less the proportion of iron, the smaller the sp. gr., and the harder the mineral on the octahedral face. The hardness is about 5·5. P. J. Holmquist obtained the following results for the cutting hardness on the octahedral faces when the hardness of quartz is 1000. The hardnesses of the samples with an asterisk are mean values for all the faces.

Sp. gr. . .	3·6	3·2	3·6	4·116	4·283	4·283
Hardness .	1779	1621	1531*	1232*	1031*	806*

The hardness decreases from that spinel proper, $Mg(AlO_2)_2$, as the proportion of iron and chromium increases. Y. Tadokoro found the coeff. of thermal expansion and sp. gr. of chromite bricks to be:

	20°	100°	250°	500°	750°	950°
Sp. gr. . .	2·982	2·978	2·966	2·945	2·925	2·910
Coeff. expansion	—	$0{\cdot}0_570$	$0{\cdot}0_597$	$0{\cdot}0_590$	$0{\cdot}0_588$	$0{\cdot}0_590$

The thermal expansions of chromite from different sources, between 20° and 1000°, in oxidizing and reducing atm., were:

	Oxidizing.	Reducing.
Rhodesian	$7{\cdot}29\times10^{-6}$	$17{\cdot}45\times10^{-6}$
African	$8{\cdot}51\times10^{-6}$	$39{\cdot}01\times10^{-6}$
Grecian	$8{\cdot}32\times10^{-6}$	$10{\cdot}06\times10^{-6}$
Indian	$7{\cdot}29\times10^{-6}$	$15{\cdot}91\times10^{-6}$

F. H. Norton gave for the thermal conductivity:

	200°	400°	600°	800°	1000°	1200°	1400°
Heat conductivity .	0·0034	0·0037	0·0039	0·0040	0·0040	0·0041	0·0041

H. Kopp found the sp. ht. of chromite to be 0·159 between 16° and 47°. E. D. Clark, and G. Spezia found that chromite fuses in the oxyhydrogen flame. A. Brun found samples of chromite with m.p., respectively, 1670° and 1850°. C. Doelter considered these results too high and gave 1450° for the m.p. of a sample from Kraubath and added that the mineral was liquid at 1600°. The m.p. of the mineral naturally depends on the proportion of iron, etc. E. S. Larsen found the index of refraction to be 2·08 to 2·10. W. W. Coblentz observed that the ultra-red reflecting power of chromite is uniformly 4 per cent. between wave-lengths 1μ and 11μ. A. de Gramont studied the spark spectrum. W. T. Wherry found chromite to be a good radio-detector. T. W. Case said that chromite is a poor electrical conductor, and the conductivity is not affected by exposure to light. K. Fischbeck and E. Einecke found the resistance to be about 22×10^4 ohms. R. D. Harvey studied this subject. Chromite is not magnetic, but it may appear to be magnetic if contaminated with magnetite. E. F. Herroun and E. Wilson gave 79×10^{-6} mass units for the magnetic susceptibility; and F. Stutzer and co-workers gave 244×10^{-6} units for the coeff. of magnetization. H. A. J. Wilkens and H. B. C. Nitze discussed the magnetic separation of chromite. E. von Federoff observed pseudomorphs of hæmatite after chromite. According to E. Zalinsky, acids are without action on chromite; finely powdered magnetite was dissolved by hydrofluoric acid under conditions where chromite was not attacked. On the other hand, G. Piolti said that 200 c.c. of sulphuric acid, mixed with an equal vol. of water, dissolved 13·42 per cent. of chromite in about 56 hrs.; and a soln. of oxalic acid in the same time formed a green soln. Y. Kato and R. Ikeno discussed the processes for decomposing chromite.

R. J. Elliot obtained dark green **cobalt chromite,** $Co(CrO_2)_2$, by precipitating a mixed soln. of equimolar parts of chrome-alum and cobalt chloride by sodium carbonate. The product is non-magnetic. G. Natta and L. Passerini obtained cobalt chromite and found that the length of unit cell of the spinel type is $a=8{\cdot}31$ A.; the vol. is 574×10^{-24} c.c.; and the sp. gr. 5·14. J. A. Hedvall heated a mixture of cobalt and chromic oxides and obtained octahedral crystals of cobalt chromite which are but little attacked by acids. K. Fischbeck and E. Einecke prepared cobalt chromite by sintering a mixture of the component oxides; and similarly also with **nickel chromite,** $Ni(CrO_2)_2$. R. J. Elliot also obtained nickel chromite by a process analogous to that used for the cobalt salt. The greyish-green nickel chromite is non-magnetic. S. Veil found that the magnetization coeff. of mixtures of the constituent oxides show maxima corresponding with the pure chromites.

REFERENCES.

[1] M. R. Nayar, H. E. Watson and J. J. Sudborough, *Journ. Indian Inst. Science,* **7**. 53, 1924; W. Herz, *Zeit. anorg. Chem.,* **28**, 344, 1901; A. Hantzsch, *ib.,* **30**. 338, 1902; W. Herz and H. W. Fischer, *ib.,* **31**. 354, 1902; **40**. 39, 1904; R. Kremann, *ib.,* **33**. 87, 1902; R. Fricke and O. Windhausen, *ib.,* **132**. 273, 1924; L. Passerini, *Gazz. Chim. Ital.,* **59**. 144, 1929; **60**. 389, 544, 1930; *Atti Accad. Lincei,* (6), **9**. 338, 1929; C. F. Nagel, *Journ. Phys. Chem.,* **19**. 569, 1915; C. F. Rammelsberg, *Pogg. Ann.,* **55**. 318, 1842; **56**. 125, 1842; **59**. 1, 1843; *Ber.,* **5**. 1003, 1872; H. B. Weiser, *The Hydrous Oxides,* New York, 76, 1926; *Colloid Symposium Wisconsin,* 38, 1923; *Journ. Phys. Chem.,* **24**. 277, 505, 1920; **25**. 665, 1921; **26**. 409, 1922; **28**. 232, 428, 1253, 1922; W. V. Bhagwat and N. R. Dhar, *Journ. Indian Chem. Soc.,* **6**. 781, 1929; E. Müller, *Zeit. angew. Chem.,* **35**. 357, 1922; M. Kreps, *Ueber salzartige Verbindungen des Chromoxyds mit Alkalien und Erden,* Berlin, 1926; M. L. Huggins, *Phys. Rev.,* (2), **21**. 509, 1923; J. K. Wood and V. K. Black, *Journ. Chem. Soc.,* **109**. 164, 1916; R. B. Corey, *Journ. Chem. Education,* **4**. 532, 1927; F. Wöhler and F. Mahla, *Liebig's Ann.,* **81**. 253, 1852; L. and P. Wöhler, *Zeit. phys. Chem.,* **62**. 445, 1908; L. and P. Wöhler and W. Plüddemann, *ib.,* **62**. 650, 1908; R. Fricke and O. Windhausen, *ib.,* **113**. 248, 1924; R. Wintgen and H. Weisbecker, *ib.,* **135**. 182, 1928; P. C. Boudault, *Liebig's Ann.,* **59**. 351, 1843; *Journ. prakt. Chem.,* (1), **36**. 23, 1845; *Journ. Pharm. Chim.,* (3), **7**. 434, 1845; M. Rosenfeld, *Ber.,* **12**. 958, 1879; **13**. 1475, 1880; F. H. Norton, *Journ. Amer. Cer. Soc.,* **10**. 30, 1927; N. Demassieux and J. Heyrovsky, *Journ. Chim. Phys.,* **26**. 219, 1929; M. Gerber, *Bull. Soc. Chim.,* (2), **27**. 435, 1877; H. Moissan, *ib.,* (3), **27**. 664, 1902; *Compt. Rend.,* **119**. 188, 1894; **134**. 160, 1912; *Ann. Chim. Phys.,* (7), **4**. 142, 1895; T. J. Pelouze, *ib.,* (3), **33**. 9, 1851; J. F. Persoz, *ib.,* (3), **25**. 283, 1849; *Compt. Rend.,* **53**. 69, 1861; S. Veil, *ib.,* **170**. 939, 1920; G. Chancel, *ib.,* **42**. 927, 1856; **43**. 927, 1856; B. Bogitch, *ib.,* **173**. 1358, 1921; E. Dufau, *ib.,* **121**. 689, 1895; **123**. 886, 1896; *Ann. Chim. Phys.,* (7), **11**. 266, 1897; (7), **12**. 263, 1897; C. H. Boehringer, *German Pat., D.R.P.* 199569, 1906; A. Mitscherlich, *Journ. prakt. Chem.,* (1), **83**. 485, 1861; E. Schweitzer, *ib.,* (1), **39**. 259, 1846; Z. Weyberg, *Centr. Min.,* 646, 1906; W. R. Nichols, *Amer. Journ. Science,* (2), **47**. 16, 1869; S. Holgersson, *Zeit. anorg. Chem.,* **192**. 123, 1930; *Lunds. Univ. Arsskr.,* (2), **23**. 9, 1929; *Fys. Selk. Handl.,* **38**. 1, 1929; C. Viard, *Bull. Soc. Chim.,* (3), **5**. 934, 1891; *Compt. Rend.,* **109**. 142, 1889; **112**. 1003, 1891; E. Mallard and J. J. Ebelmen, *ib.,* **105**. 1261, 1887; J. J. Ebelmen, *Mém. Savans Etranger,* **13**. 532, 1852; *Ann. Mines,* (5), **2**. 335, 1852; (5), **4**. 173, 1853; *Phil. Mag.,* (3), **31**. 311, 1847; **22**. 324, 1852; M. Gröger, *Monatsh.,* **25**. 520, 1904; *Sitzber. Akad. Wien,* **81**. 534, 1880; F. de Carli, *Atti Accad. Lincei,* (6), **1**. 533, 1925; F. Hein and H. Meininger, *Zeit. anorg. Chem.,* **145**. 95, 1925; K. Fischbeck and E. Einecke, *ib.,* **167**. 21, 1927; H. P. Cady and R. Taft, *Journ. Phys. Chem.,* **29**. 1075, 1925; E. S. Simpson, *Min. Mag.,* **19**. 99, 1920; K. S. Nargund and H. E. Watson, *Journ. Indian Inst. Science,* **9**. 149, 1926; F. L. S. Jones, *Journ. Ind. Eng. Chem.,* **15**. 75, 1923; T. S. Hunt, *Rep. Geol. Sur. Canada,* 73, 1850; T. Petersen, *Journ. prakt. Chem.* (1), **106**. 137, 1869; E. Glasser, *Ann. Mines,* (10), **4**. 299, 1903; (10), **5**. 29, 503, 1904; A. Damour, *Bull. Soc. Géol.,* **29**. 413, 1862; A. Hilger, *Neues Jahrb. Min.,* 399, 1866; C. Friedheim, *ib.,* ii, 156, 1891; F. Sandberger, *ib.,* 388, 1866; G. C. Hoffmann, *Amer. Journ. Science,* (4), **13**. 242, 1902; B. Kosmann, *Ber. Niederrh. Ges. Bonn.,* 144, 1869; *Zeit. deut. geol. Ges.,* **44**. 359, 1892; M. Websky, *ib.,* **25**. 394, 1873; F. Beijerinck, *Neues. Jahrb. Min. B.B.,* **11**. 455, 1898; J. C. Delamétherie, *Théorie de la terre,* Paris, **2**. 281, 1797; P. Picot de la Peyrouse, *Mém. Acad. Toulouse,* **3**. 410, 1829; T. Thomson, *Outlines of Mineralogy, Geology, and Mineral Analysis,* London, **1**. 214, 1836; G. M. Bock, *Ueber einige schlesische Mineralien deren Constitution und einige andere analytische Resultate,* Breslau, 1868; A. Breithaupt, *Vollständige Charakteristik des Mineralsystems,* 234, 1832; S. H. C. Briggs, *Journ. Chem. Soc.,* 242, 1929; J. d'Ans and J. Löffler, *Ber.,* **63**. B, 1446, 1930; W. Biltz, A. Lemke and K. Meisel, *Zeit. anorg. Chem.,* **186**. 373, 1930; E. W. Flosdorf and G. B. Kistiakowsky, *Journ. Phys. Chem.,* **36**. 1907, 1930.

[2] L. Duparc and S. P. de Rubies, *Bull. Soc. Min.,* **36**. 20, 1913; H. B. Maufe, B. Lightfoot

and A. E. V. Zeally, *Bull. South Rhodesia Geol. Sur.*, 8, 1919 ; A. Hofmann, *Ueber das Chromerzvorkommen in Ungarn und dessen Aufschliersen*, Rostock, 1873 ; G. Tschermak, *Trav. Musée Acad. St. Petersburg*, **6**. 49, 1913 ; A. de Launay, *Formation des gites métallifères*, Paris, 1883 ; H. E. Kramm, *Proc. Amer. Phil. Soc.*, **49**. 315, 1916 ; C. Camsell, *Econ. Geol.*, **6**. 604, 1911 ; A. Christomanos, *Ber.*, **10**. 543, 1877 ; P. Niggli, *Allgemeine Mineralogie*, Berlin, 622, 1926 ; *Spezielle Mineralogie*, Berlin, 135, 1926 ; H. Schneiderhöhn, *Anleitung zur mikroskopischen Untersuchungen von Erzen*, Berlin, 263, 1922 ; G. Piolti, *Ann. Accad. Torino*, **40**. 114, 1905 ; B. Simmersbach, *Berg. Hütt. Ztg.*, **63**. 52, 1904 ; R. Helmhacker, *ib.*, **56**. 31, 1897 ; V. Hilber and I. Ippen, *Neues Jahrb. Min. B.B.*, **18**. 52, 1904 ; E. von Federoff and W. Nikitin, *Ann. Géol. Min. Russie*, **3**. 91, 1899 ; M. P. Melnikoff, *Proc. Russ. Min. Soc.*, 375, 1888 ; A. Rocati, *Bol. Soc. Geol. Ital.*, **20**. 124, 1901 ; A. Stella, *ib.*, **43**. 182, 1924 ; W. Wallace and R. M. Clark, *Bull. South Rhodesia Geol. Sur.*, **3**. 88, 1919 ; M. Z. Jovicic, *Sitzber. Akad. Wien*, **117**. 823, 1908 ; *Bull. Soc. Min.*, **35**. 511, 1912 ; S. G. Gordon, *Proc. Acad. Phil.*, **73**. 449, 1921 ; J. S. Diller, *Trans. Amer. Inst. Min. Eng.*, **63**. 105, 1915 ; W. G. Maynard, *ib.*, **27**. 283, 1907 ; H. E. Williams, *Eng. Min. Journ.*, **111**. 375, 1921 ; P. Kato, *Journ. Geol. Soc. Tokyo*, **28**. 1, 1921 ; L. F. Lubogetzky, *Metall Erz*, **22**. 51, 1922 ; O. Stutzer, *ib.*, **17**. 249, 1920 ; E. Berwerth, *Zeit. Kryst.*, **38**. 320, 1904 ; L. Tokody, *ib.*, **67**. 338, 1928 ; *Mat. Termes Zett. Ertasito Budapest*, **45**. 278, 1928 ; E. Cohen and E. Weinschenk, *Ann. Nat. Hist. Mus. Wien*, **5**. 131, 1891 ; E. Kaiser, *Neues Jahrb Min.*, i, 357, 1927 ; B. Baumgärtel, *Tschermak's Mitt.*, (2), **23**. 397, 1904 ; A. Himmelbauer, *ib.*, (2), **32**. 136, 1914 ; F. Beyschlag, P. Krusch and J. H. L. Vogt, *Die Lagerstätten der nutzbaren Mineralien und Gesteine*, Stuttgart, **1**. 265, 1914 ; F. Stromeyer, *Gilbert's Ann.*, **42**. 105, 1812 ; C. F. Rammelsberg, *Sitzber. Akad. Berlin*, 245, 1844 ; *Pogg. Ann.*, **62**. 458, 1844 ; F. Wöhler, *Sitzber. Akad. Wien*, **46**. 303, 1862 ; G. Tschermak, *ib.*, **61**. 468, 1870 ; **88**, 362, 1883 ; G. Rose, *Sitzber. Akad. Berlin*, 80, 88, 115, 123, 139, 1863 ; N. S. Maskelyne, *Phil. Trans.*, **160**, 189, 1870 ; **161**. 359, 1871 ; V. Wartha, *Zeit. anal. Chem.*, **17**. 433, 1878 ; L. Fletcher, *Min. Mag.*, **7**. 183, 1887 ; O. W. Huntington, *Proc. Amer. Acad.*, **26**. 6, 1891 ; H. B. von Foullon, *Ann. Hofmuseums Wien*, **3**. 195, 1888 ; A. Eberhard, *Arch. Naturk. Dorpat*, **9**. 137, 1882 ; T. N. Tschernyschoff, *Zeit. deut. geol. Ges.*, **35**. 191, 1883 ; A. Daubrée, *Compt. Rend.*, **62**. 77, 1866 ; **91**. 30, 1880 ; S. Veil, *ib.*, **188**. 330, 1929 ; R. D. M. Verbeek, *Jaarboek. Nederlandsch Oost-Indië*, **1**. 15, 1886 ; E. Cohen, *Meteoritenkunde*, Stuttgart, **1**. 244, 1894 ; H. Forestier and G. Chaudron, *Compt. Rend.*, **180**. 1264, 1925 ; H. A. J. Wilkens and H. B. C. Nitze, *Trans. Amer. Inst. Min. Eng.*, **26**. 351, 1896 ; L. N. Vauquelin, *Bull. Soc. Philomath.*, 55, 1800 ; P. Meder, *Crell's Ann.*, i. 500, 1798 ; D. L. G. Karsten, *Mineralogische Tabellen*, Berlin, 56, 1800 ; **74**. 1808 ; J. J. N. Huot, *Manuel de minéralogie*, Paris, **1**. 287, 1841 ; E. J. Chapman, *Practical Mineralogy*, London, 1843 ; C. F. Rammelsberg, *Handbuch der Mineralchemie*, Leipzig, 142, 1875 ; **2**. 61, 1895 ; W. Haidinger, *Handbuch der bestimmenden Mineralogie*, Wien, 550, 1845 ; A. Breithaupt, *Vollständige Charakteristik des Mineralsystems*, Dresden, 234, 1832 ; E. V. Shannon, *Amer. Min.*, **11**. 16, 1926 ; M. Websky, *Zeit. deut. geol. Ges.*, **25**. 394, 1873 ; F. C. Hochstetter, *ib.*, **16**. 341, 1864 ; H. Traube, *ib.*, **46**. 581, 1894 ; A. Arzruni, *ib.*, **37**. 865, 1885 ; G. M. Bock, *Ueber einige schlesische Mineralien deren Constitution und einige andere analytische Resultate*, Breslau, 1868 ; E. D. Clark, *The Gas Blowpipe*, London, 74, 1819 ; T. Petersen, *Journ. prakt. Chem.*, (1), **106**. 137, 1869 ; J. J. Ebelmen, *Mém. Savans Étranger*, **13**. 532, 1852 ; *Ann. Mines*, (5), **2**. 335, 1852 ; (5), **4**. 173, 1853 ; *Phil. Mag.*, (3), **31**. 311, 1847 ; *Ann. Chim. Phys.*, (3), **32**. 211, 1848 ; (3), **33**, 44, 1851 ; *Edin. Phil. Journ.*, **44**. 311, 1848 ; **22**. 324, 1852 ; H. Kopp, *Liebig's Ann. Suppl.*, **3**. 294, 1865 ; H. Arsandaux, *Bull. Soc. Min.*, **48**. 70, 1925 ; A. Michel-Lévy, *ib.*, **1**. 135, 1878 ; F. Fouqué and A. Michel-Lévy, *Synthèse des minéraux*, Paris, 250, 1882 ; S. Meunier, *Bull. Soc. Min.*, **10**. 187, 1887 ; *Compt. Rend.*, **107**. 1153, 1888 ; **110**. 424, 1890 ; B. Bogitsch, *ib.*, **173**. 1358, 1921 ; A. de Gramont, *ib.*, **126**. 1513, 1898 ; J. Clouet, *ib.*, **78**. 762, 1868 ; *Ann. Chim. Phys.*, (4), **16**. 90, 1869 ; M. Gerber, *Bull. Soc. Chim.*, (2), **27**. 435, 1877 ; H. Moissan, *Le chrome et ses composés*, Paris, 1884 ; J. A. Hedvall, *Svenska Kem. Tids.*, **37**. 166, 1925 ; *Zeit. anorg. Chem.*, **93**. 313, 1915 ; R. J. Elliot, *On magnetic combinations with some observations of the action of selenic acid on methyl alcohol*, Göttingen, 33, 1862 ; W. W. Coblentz, *Investigations of Infra-red Spectra*, Washington, **5**. 15, 1908 ; W. T. Wherry, *Amer. Min.*, **10**. 28, 1925 ; K. Fischbeck and E. Einecke, *Zeit. anorg. Chem.*, **167**. 21, 1927 ; **175**. 335, 1928 ; Y. Tadokoro, *Science Rep. Tohoku Univ.*, **10**. 339, 1921 ; P. F. Kerr, *Econ. Geol.*, **19**. 1, 1924 ; T. W. Case, *Phys. Rev.*, (2), **9**. 305, 1917 ; A. Lacroix, *Bull. Soc. Min.*, **43**. 69, 1920 ; G. Spezia, *Atti Accad. Torino*, **22**. 419, 1887 ; L. Colomba, *ib.*, **31**. 593, 1896 ; C. Doelter, *Centr. Min.*, 200, 1902 ; *Mineralschätze der Balkanländer*, Stuttgart, 116, 1916 ; *Tschermak's Mitt.*, (2), **11**. 319, 1890 ; (2), **22**. 316, 1902 ; A. Brun, *Arch. Sciences Genève*, (4), **13**. 352, 1902 ; H. Abich, *Pogg. Ann.*, **23**. 345, 1831 ; *De spinello*, Berolensis, 1831 ; A. Moberg, *Journ. prakt. Chem.*, (1), **43**. 114, 1848 ; (1), **44**. 322, 1848 ; A. Laugier, *Ann. Mus. Hist. Nat.*, **6**. 325, 1804 ; **7**. 392, 1806 ; *Ann. Chim. Phys.*, (1), **78**. 69, 1881 ; *Nicholson's Journ.*, **32**. 78, 1812 ; *Phil. Mag.*, **24**. 4, 1806 ; M. H. Klaproth, *ib.*, **1**. 78, 1798 ; *Gehlen's Journ.*, i, 189, 1806 ; *Ann. Chim. Phys.*, (1), **25**. 273, 337, 1798 ; *Journ. Mines*, **7**. 145, 1798 ; *Nicholson's Journ.*, **2**. 372, 1799 ; J. Thoulet, *Bull. Soc. Min.*, **2**. 34, 1879 ; E. Hussak, *Zeit. Kryst.*, **30**. 398, 1899 ; *Neues Jahrb. Min.*, ii, 27, 1898 ; G. Sukkow, *ib.*, 647, 1834 ; E. von Federoff, *ib.*, i, 345, 1900 ; J. H. L. Vogt, *Zeit. prakt. Geol.*, **2**. 381, 1894 ; **6**. 731, 1898 ; C. Hütter, *ib.*, **28**. 53, 1920 ; F. Ryba, *ib.*, **8**. 339, 1900 ; F. Zirkel, *ib.*, **1**. 89, 1893 ; F. W. Voit, *ib.*, **16**. 137, 191, 1908 ; O. Weiss, *ib.*, **9**. 250, 1901 ; J. H. Pratt, *Amer. Journ. Science*, (4), **7**. 181, 1899 ; J. C. Booth and C. Lea, *ib.*, (1), **38**. 243, 1840 ; H. Seybert, *ib.*, (1),

4. 321, 1822; T. H. Garrett, *ib.*, (2), **14**. 45, 1852; (3), **15**. 332, 1853; E. Bechi, *ib.*, (2), **19**. 119, 1855; G. C. Hoffmann, *ib.*, (4), **13**. 242, 1902; F. H. Norton, *Journ. Amer. Cer. Soc.*, **10**. 30, 1927; R. D. Harvey, *Econ. Geol.*, **23**. 778, 1928; G. Natta and L. Passerini, *Gazz. Chim. Ital.*, **59**. 280, 1929; J. L. Smith, *Compt. Rend.*, **92**. 981, 1881; *Amer. Journ. Science*, (3), **21**. 461, 1881; C. U. Shepard, *ib.*, (2), **2**. 382, 1846; (2), **15**. 365, 1853; G. F. Kunz, *ib.*, (3), **34**. 477, 1887; E. Zalinsky, *Centr. Min.*, 647, 1902; N. Federowsky, *ib.*, 76, 1927; R. Brauns, *ib.*, 266, 1927; J. Königsberger, *ib.*, 565, 597, 1908; A. Knop, *Ber. Oberrh. Geol. Ver.*, **22**. 10, 1889; **23**. 20, 1890; *Neues Jahrb. Min.*, 697, 1877; T. Wada, *Minerals of Japan*, Tokyo, 1904; E. Divers, *Chem. News*, **44**. 217, 1881; H. Pemberton, *ib.*, **63**. 46, 1891; R. W. E. MacIvor, *ib.*, **57**. 1, 1888; L. E. Rivot, *Ann. Chim. Phys.*, (3), **30**. 20, 1850; P. Berthier, *ib.*, (3), **17**. 50, 1846; (3), **33**. 34, 1851; L. Cascuel, *Ann. Mines*, (9), **20**. 5, 1901; F. Kovar, *Abhand. Böhm, Akad.*, 27, 1900; A. Liversidge, *Proc. Roy. Soc. New South Wales*, **16**. 39, 1800; **20**. 73, 1887; K. von John and C. F. Eichleiter, *Jahresb. geol. Reichsanst. Wien*, **53**. 481, 1903; F. W. Clarke, *Bull. U.S. Geol. Sur.*, 419, 1910; E. S. Larsen, *ib.*, 679, 1921; J. H. Lewis, *ib.*, 725, 1922; A. C. Gill, *ib.*, 742, 1922; G. P. Merrill, *Journ. Washington Acad.*, **2**. 41, 1912; L. H. Borgström, *Geol. För. Förh. Stockholm*, **30**. 331, 1908; P. J. Holmquist, *ib.*, **42**. 303, 1923; **44**. 485, 1922; G. T. Prior, *Min. Mag.*, **18**. 1, 1916; E. S. Simpson, *ib.*, **19**. 99, 1920; W. Tassin, *Proc. U.S, Nat. Museum*, **34**. 685, 1908; A. E. V. Zeally, *Trans. Geol. Soc. South Africa*, **17**. 72, 1914; P. A. Wagner, *ib.*, **26**. 1, 1923; H. S. Harger, *ib.*, **6**. 110, 1905; L. W. Fisher, *Amer. Min.*, **14**. 341, 1929; *Econ. Geol.*, **24**. 621, 1929; F. E. Keep, *ib.*, **25**. 219, 425, 1930; C. S. Ross, *ib.*, **24**. 632, 1929; J. E. Singewald, *ib.*, **24**. 632, 1929; C. Sandonnini, *Gazz. Chim. Ital.*, **60**. 321, 1930; Anon., *Journ. Franklin Inst.*, **210**. 382, 1930; Y. Kato and R. Ikeno, *Journ. Japan. Soc. Chem. Ind.*, **33**. 225, 1930; G. Grenet, *Ann. Physique*, (10), **13**. 263, 1930; G. M. Schwartz, *Econ. Geol.*, **24**. 592, 1929; E. Sampson, *ib.*, **24**. 632, 1929; A. Hilger, *Neues Jahrb. Min.*, 385, 1866; L. Passerini, *Gazz. Chim. Ital.*, **60**. 544, 1930; S. Holgersson, *Lunds Univ. Arsskr.*, (2), **23**. 9, 1929; *Fys. Selk. Handl.*, **38**. 1, 1929; F. Stutzer, W. Gross and K. Bornemann, *Metall Erz*, **6**. 1, 1918; E. F. Herroun and E. Wilson, *Proc. Phys. Soc.*, **33**. 196, 1921; P. E. Wretblad, *Zeit. anorg. Chem.*, **189**. 329, 1930.

§ 12. Intermediate Chromium Oxides

A number of oxides, with compositions intermediate between those of chromic oxide, Cr_2O_3, and chromic anhydride, CrO_3, has been reported. These oxides include Cr_5O_9, Cr_3O_5, Cr_3O_6, Cr_5O_{13}, Cr_5O_{12}, and Cr_6O_{15}. They are sometimes represented as *chromium chromates*. Their individuality is not well established. K. Honda heated chromium trioxide in an apparatus recording the losses in weight in terms of the movement of an indicator on a scale. There is first the expulsion of moisture, and, at about 300°, Cr_6O_{15} is formed; then, at 420°, Cr_5O_9; and, at about 450°, chromic oxide, Cr_2O_3. The results agree with the magnetic observations of K. Honda and T. Sone,[1] who found that at about 280°, Cr_6O_{15} is formed and at 420°, Cr_2O_3; while between 300° and 400°, the strongly paramagnetic Cr_6O_{15}, and the ferromagnetic Cr_5O_9 are present as a mixture. A. Simon and T. Schmidt could not obtain these oxides. They observed only two intermediate oxides, as illustrated by Fig. 22, namely, **chromium pentitatridecoxide,** Cr_5O_{13}, and chromium pentitadodecoxide, Cr_5O_{12}. The other intermediate oxides reported in the literature either do not exist or are too unstable to appear under these conditions.

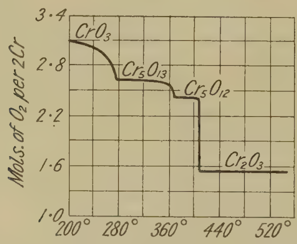


FIG. 22.—Losses in Weight on Heating Chromium Trioxide.

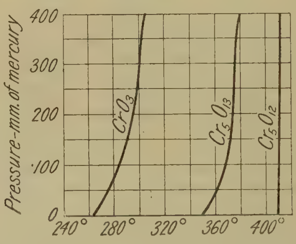


FIG. 23.—Dissociation Pressure Curves of the Chromium Oxides.

The first member, **chromium pentitenneaoxide,** Cr_5O_9, or $2Cr_2O_3.CrO_3$, was obtained by F. Wöhler by passing the vapour of chromyl chloride through a tube at a temp. between 300° and dull redness. If the temp. be too high, free chromic oxide is formed; and A. Geuther and V. Merz said that if it be too low, free chromic anhydride will be present. A. Geuther and V. Merz also obtained a small yield of this oxide by heating chromic anhydride alone, or in a current of oxygen. According to O. Popp, an *enneahydrate*, $2Cr_2O_3.CrO_3.9H_2O$, is produced as a brown mass when a soln. of sodium thiosulphate, with potassium dichromate is boiled. E. Kopp said that this product is the Cr_8O_{15}-oxide. According to L. Blanc, if precipitated chromic oxide, α-Cr_2O_3, be heated to 230° for some time it passes into chromium dioxide, CrO_2, and if this product be hydrolyzed, it forms amorphous or α-Cr_5O_9; and if this product be heated between 350° and 400°, it forms a mixture of crystalline or β-Cr_5O_9, and β-Cr_2O_3. At 450°, this reaction is instantaneous with the evolution of much heat. At 300°, the reaction $2\alpha\text{-}Cr_5O_9+O_2\rightarrow 10CrO_2$ occurs; and at 350°, $10CrO_2\rightarrow 2Cr_5O_9+O_2$. According to L. Blanc, if a salt of tervalent aluminium, iron, or chromium be added to a soln. of a neutral chromate, and the precipitate be washed with boiling water, yellow aluminium chromate, $2Al_2O_3.CrO_3$; or brown ferric chromate, $2Fe_2O_3.CrO_3$; or brown chromic chromate, $2Cr_2O_3.CrO_3$, is formed as the case may be. It is therefore inferred that the pentita-enneaoxide is a chromic chromate. L. Blanc and G. Chaudron assumed that there are two forms of Cr_5O_9 with a transition temp. at 440°—*vide supra*, chromic oxide. A. Geuther and V. Merz observed that the Cr_5O_9-oxide furnishes rhombic prisms paler in colour than chromic oxide, and having a violet tinge. The sp. gr. is 4·0 at 10°; and they considered that F. Wöhler's amorphous, black powder was probably the impure oxide. F. Wöhler said that the compound is magnetic, but, added E. Wedekind and K. Fetzer, not so magnetic as manganese phosphide. While F. Wöhler thought the magnetic oxide of chromium is Cr_3O_4; A. Geuther and V. Merz, Cr_5O_9; and I. Schukoff, Cr_4O_9, L. Blanc showed that the magnetic oxide is probably an unstable variety of Cr_5O_9 intermediate between the α- and β-forms. The magnetic susceptibility with between 0 and 200 gauss is nearly equal to that of magnetite. K. Honda and T. Sone gave for the magnetic susceptibility, χ, with a field of strength H gauss:

H . . .	294	646	1306	2012	3064	6682	9260
χ . . .	718	640	487	408	300	137	99

According to I. Schukoff, the intermediate oxides obtained by heating chromyl chloride or chromic anhydride are magnetic or not, according to the conditions. If the decomposition is controlled so that the temp. does not rise above 500°, the oxides obtained are only feebly magnetic. On heating, however, to 500°–510°, 13–14 per cent. of oxygen is evolved, and the black mass, which has the composition $2CrO_3.Cr_2O_3$, is strongly magnetic. An oxide of the same composition, but prepared at 450°, was very feebly magnetic. A crystalline magnetic oxide was obtained by the decomposition of chromyl chloride; when ignited, it loses only 3·4–4 per cent. of oxygen. According to F. Wöhler, the Cr_5O_9-oxide is reduced to chromic oxide when heated in hydrogen; and when heated in air, it forms green chromic oxide, and is then no longer magnetic. A. Geuther and V. Merz also found that the oxide is slowly reduced to chromic oxide when heated in air; it is insoluble in hydrochloric and nitric acids, in aqua regia, and in a mixture of nitric and hydrofluoric acids; boiling alkali-lye slowly decomposes it into chromic oxide and chromic anhydride; and it is easily decomposed by fused alkali hydroxides.

According to M. Traube,[2] when chromic anhydride is exposed on a glass plate, it dries to a brown crust which is insoluble in water, and adheres strongly to the glass. Its composition agrees with **chromium octitapentadecaoxide**, Cr_8O_{15}, or $2Cr_2O_3.3CrO_3$; and it is supposed to be produced by the action of the dust in the air. It can be obtained by treating a moderately dil. soln. of chromic acid at ordinary temp. with an excess of alcohol, and heating the mixture after the evolution of aldehyde has ceased. Part of the oxide settles quickly and part remains in suspension for some weeks. The precipitate is boiled until the smell of acetic is evident, then agitated with water, and lastly with alcohol until nothing is dissolved out by either liquid. The dried product is a greenish-brown powder; before drying, the product is readily dissolved in hydrochloric and nitric acids, and alkali-lye, but less readily in acetic acid. Ammonia precipitates hydrated chromic oxide from the soln. in acids. A. Simon and T. Schmidt observed that when $Cr_8O_{15}.nH_2O$ is heated, water and oxygen are simultaneously given off between 100° and 400°. The brown powder obtained by C. F. Rammelsberg by mixing soln. of chrome-alum and potassium dichromate was considered to be the *enneahydrate*, $2Cr_2O_3.3CrO_3.9H_2O$; but C. W. Eliot and F. H. Storer showed that it is probably a mixture.

L. N. Vauquelin[3] prepared brown oxide of chromium, or **chromium dioxide,** $Cr_2O_3.CrO_3$, or Cr_2O_4, or CrO_2, or *chromyl chromate*, $(CrO)_2CrO_4$, by heating chromic nitrate until all the nitric acid is expelled, repeating the treatment with nitric acid, and finally heating the product short of redness; F. Brandenburg employed a similar process. M. Z. Jovitschitsch heated the nitrate to 290°; and L. Blanc heated amorphous chromic oxide to 280°—*vide supra.* A. Maus added that the temp. required to expel all the nitric acid results in the formation of chromic oxide. The product obtained by heating hydrated chromic oxide below redness, in air—to 200°–250°, according to H. Löwel—is, according to M. Krüger, chromium dioxide but C. W. Eliot and F. H. Storer, and M. Siewert said that this product is only a mixture. H. Moissan, and W. Manchot prepared this oxide by heating hydrated chromic oxide to 330°–440° in a current of oxygen; M. Z. Jovitschitsch said that anhydrous chromium chromate cannot be prepared by heating the hydrated oxide since decomposition occurs before the last mol. of water is expelled. G. N. Ridley obtained it by heating chromic anhydride to 250°; by passing sulphur dioxide over heated chromic anhydride; and by gently heating a mixture of chromic anhydride and phosphorus in a crucible until all takes fire. E. Moles and F. Gonzalez prepared the dioxide by heating ammonium dichromate to 225°; and E. Maumené, by heating ammonium chromate to 204°.

A number of hydrates of chromium dioxide has been reported. According to C. W. Eliot and F. H. Storer, the compound is not produced by boiling an aq. soln. of ammonium chromate; nor as indicated by L. N. Vauquelin, and H. Moser, by passing chlorine through a soln. of a chromic salt, and precipitating with potash-lye; nor, as indicated by H. Schiff, by treating hydrated chromic oxide, or violet chromic chloride with bleaching powder. K. Seubert and J. Carstens assumed that chromium dioxide is formed as an intermediate stage in the reduction of chromic anhydride by an iodide, or by hydrazine; but R. Luther and T. F. Rutter preferred the assumption that the reduction proceeds through stages involving sexi-, quinque-, quadri-, and ter-valent chromium. The reaction was also discussed by W. L. Miller. According to A. Maus, hydrated chromium dioxide is formed by digesting hydrated chromic oxide with a soln. of chromic acid—not in excess. A. Maus obtained it by digesting a hot soln. of potassium chromate with chromic chloride, A. Bensch, with chromic sulphate, and C. W. Eliot and F. H. Storer, with chrome-alum. E. Schweitzer, P. Grouvelle, and C. W. Eliot and F. H. Storer treated a soln. of potassium dichromate with nitric oxide; O. Popp, and E. Kopp, with sodium thiosulphate; G. N. Ridley, with stannous chloride; A. Vogel, and L. Godefroy, with alcohol; J. W. Swan, with organic substances; and H. Schiff, with oxalic acid. T. E. Thorpe obtained it by treating a soln. of chromium hexoxydichloride with ammonia. P. A. Meerburg found that colloidal chromium dioxide is formed when a soln. of chromic acid is treated with potassium iodide. The colloid is slowly modified with a decreased absorptive power. The amount of water absorbed over conc. sulphuric acid at ordinary temp. is greater than at 100°. A rise of temp. over 100° increases the loss of water, and decreases the absorptive power.

According to A. Vogel, the product dried at 100° is the *dihydrate*, $CrO_2.2H_2O$, while L. Godefroy represented it as a *hemitrihydrate*, $CrO_2.1\frac{1}{2}H_2O$, which he symbolized $(HO)_3{\equiv}Cr-O-Cr{\equiv}(OH)_3$. W. M. Horton found that by heating ammonium dichromate in air below 190° a *hemihydrate*, $2CrO_2.H_2O$, is formed as a black powder. J. J. Berzelius supposed the brown oxide prepared by L. N. Vauquelin to be a definite oxide; T. Thomson, and J. M. Godon de St.

Menin seem to have regarded it as a mixture of chromic oxide and chromic anhydride; and J. F. John, C. W. Eliot and F. H. Storer, J. W. Döbereiner, and A. Maus, as a feeble compound of green chromic oxide and chromic acid—namely, chromium chromate. According to M. Z. Jovitschitsch, when a soln. of chromic oxide in nitric acid is evaporated until excess of acid is removed and the residue is dissolved in water and treated with ammonia, a dark brown, almost black product is obtained, analyses of which are in agreement with the formula, $Cr_2(OH)_8.H_2O$, or $CrO_3.Cr_2O_3.7H_2O$. The loss of $1H_2O$ over sulphuric acid, of $2H_2O$ at 105°, and of $6H_2O$ at 205° is more readily explained by the former, but the chromium content and particularly the possibility of the preparation of anhydrous chromium chromate from the substance, favour the formula $Cr_2O_3.CrO_3.7H_2O$. The analytical data agree equally well with those required for the peroxide, CrO_2, but the readiness with which the substance is converted by ammonia, alkali carbonate, or hydroxide or by boiling water into chromium hydroxide and chromate is interpreted in favour of a salt-like constitution. W. Manchot and R. Kraus said that the product obtained by heating chromic hydroxide to 320° to 345° for several hrs. is a hygroscopic, black powder containing 6 to 7 per cent. of water. Its general properties are those of a peroxide and not of a chromic chromate, and the formula is probably $O : Cr : O$. It thus differs from the peroxide, $O : Cr.O.O.Cr : O$, which appears as the primary product of the autoxidation of chromous oxide. The existence of this chromium dioxide is regarded as evidence in favour of the view that chromium is quadrivalent in chromium trioxide. A. Simon and T. Schmidt observed that oxygen is given off, and the dioxide passes into chromic oxide at 380°. E. Moles and F. Gonzalez gave for the magnetic susceptibility $42{\cdot}2\times10^{-6}$ units.

Chromium dioxide is a dark grey, almost black, solid which gives off oxygen at 300° forming green chromic oxide. L. and P. Wöhler said that the decomposition of chromium dioxide in vacuo begins at about 280°. When prepared by igniting hydrated chromic oxide, W. Manchot and R. Kraus found that it contained 6 or 7 per cent. of water which is evolved along with oxygen at a red-heat, and chromic oxide remains. E. Hintz found that when heated with **chlorine,** at about 250°, it forms chromic and chromyl chlorides; when treated with **water,** it forms no chromic acid; but M. Martinon found that with **hydrogen dioxide,** oxygen is rapidly evolved at 68°, and the addition of a few drops of sulphuric acid results in the formation of blue perchromic acid. This agrees with the hypothesis that the dioxide is chromium chromate. H. Moissan, and W. Manchot and R. Kraus found that it reacts slowly with **hydrochloric acid** liberating chlorine; and it likewise reacts with **hydriodic acid** liberating iodine. M. Krüger said that with a mixture of pyrosulphuric acid and **sodium chloride,** chlorine and not chromyl chloride is formed; and with conc. sulphuric acid and sodium chloride, C. W. Eliot and F. H. Storer obtained chromyl chloride. H. Moissan, O. Popp, etc., found that it is soluble in **sulphuric acid.** W. Manchot and R. Kraus found that when warmed with **sulphur dioxide,** sulphur trioxide is formed; and warm **sulphurous acid** is converted into sulphuric acid. C. W. Eliot and F. H. Storer, O. Popp, etc., observed that chromic dioxide readily dissolves in dil. **nitric acid;** the soln. is reddish-brown, and gives a dirty green precipitate with ammonia. W. Manchot and R. Kraus found that conc. nitric acid converts the dioxide into chromic acid. E. Hintz found that it is scarcely attacked by **phosphorus pentachloride** at 250°. A. Maus stated that a little **arsenic acid** converts the dioxide into chromic arsenate, which is soluble in an excess of arsenic acid. The dioxide is insoluble in **ether, acetone,** and other organic liquids; and O. Popp said that the dioxide dissolves with difficulty in **acetic acid.** M. Krüger, W. Manchot and R. Kraus, etc., observed that boiling **potassium** or **sodium hydroxide** converts the dioxide into a soln. of alkali chromate, and a precipitate of hydrated chromic oxide. This simultaneous oxidation and reduction furnishes an illustration of the acidic and basic properties of chromium dioxide. A. Maus found that when digested with **lead acetate** in the presence of acetic acid, lead chromate and chromic acetate are formed. E. Maumené said that the brown oxide is soluble in aq. **chromic acid,** or in soln. of **alkali dichromates,** and when the brown soln. are diluted with water, the brown oxide is re-precipitated.

I. Schukoff[4] heated chromic anhydride to 500°–510° and obtained *chromium tetritaenneaoxide*, Cr_4O_9, or $Cr_2O_3.2CrO_3$. The magnetic qualities of this substance disappear at 120°–130°, and reappear on cooling. For $Cr_2O_3.6CrO_3$, *vide infra*, chromium dichromate. For **chromium pentitatridecoxide,** Cr_5O_{13}, *vide supra*. The heating curve of A. Simon and T. Schmidt is shown in Fig. 22, and the dissociation press. in Fig. 23. According to J. W. Döbereiner, and M. Traube, **chromium pentitadodecoxide,** Cr_5O_{12}, or $Cr_2O_3.3CrO_3$, *i.e.* normal *chromium chromate*, or *chromic chromate*, $Cr_2(CrO_4)_3$, is formed when chromic anhydride is heated to about 250°. By boiling the product with water, or after standing a long time in contact with that liquid, it is converted into a soluble modification. The other reactions resemble those obtained with the preceding oxide. A. Simon and T. Schmidt's heating curve is shown in Fig. 22, and the dissociation press. curve in Fig. 23. G. Rothaug's observations were discussed in connection with the oxidation of chromic oxide. S. Takegami observed that chromic chromate is sometimes deposited in a colloidal form on the cathode during the electrolysis of soln. of chromic acid. This occurs when the ratio of ter- to sexivalent chromium is 1 : 0·5. Observations were previously made by E. Müller and co-workers who regard the film as $Cr_2(OH)_4CrO_4$—*vide supra*, the deposition of chromium. A. Maus found that *chromium hexitapentadecaoxide*, Cr_6O_{15}, or $Cr_2O_3.4CrO_3$, is formed when a hydrated chromic oxide or chromic carbonate is dissolved in a cold, aq. soln. of chromic acid, and the soln. evaporated. The brittle, horny product is permanent in air, and dissolves without change in alcohol; the soln. may be evaporated a number of times at 100° without decomposition, but A. A. Hayes observed that if kept for a long time at that temp. the compound becomes insoluble. K. Honda and co-workers obtained this product by heating chromium trioxide to 280°, and they said that its magnetic susceptibility at room temp. is $14{\cdot}2\times10^{-6}$. C. D. Braun treated a conc. aq. soln. of potassium ferrocyanide with potassium dichromate, and on evaporation obtained a resinous mass of the *dodecahydrate*, $Cr_6O_{15}.12H_2O$.

C. W. Eliot and F. H. Storer summed up the result of their examination of these intermediate oxides by saying: "There is not a particle of evidence of the existence of any chromate of chromium containing more than one equivalent of chromic acid." The position is very nearly the same to-day.

According to J. Heintze,[5] by passing a slow current of ammonia into a dil. chloroform soln. of chromyl chloride and by evaporating the solvent, there remains brown **ammonium chromochromate,** $NH_4O.CrO_2.O.Cr.O.CrO_2.ONH_4$, which loses water and ammonia when heated, forming chromic oxide. The salt forms a brownish-yellow soln. with water, but it is insoluble in alcohol, ether, chloroform, and glacial acetic acid; it dissolves in conc. acids, and the acid soln., when diluted with water, deposits the original salt as a brown powder. The salt is decomposed by soda-lye, giving off ammonia. J. Heintze prepared **potassium chromochromate** in an analogous manner, but neither A. Leist, nor A. Werner and A. Klein could verify this. D. Tommasi reported **potassium chromic hydroxychromate,** $K_2CrO_4.2Cr(OH)CrO_4$, to be formed by the action of nitric oxide on a soln. of one part of potassium dichromate in 2 parts of fuming nitric acid, at 70°; evaporating the product to dryness on a water-bath; extracting with hot water; and drying at 150°. The violet-brown, amorphous powder is without taste or smell; its sp. gr. at 14° is 2·28; it melts at 300°, and decomposes: $K_2CrO_4.2Cr(OH)CrO_4 = 2Cr_2O_3 + K_2CrO_4 + H_2O + 3O$. When mixed with potassium chlorate it does not detonate by percussion, but it burns vigorously when heated. It is insoluble in water, alcohol, and acetic acid; conc. nitric acid has very little action in the cold, but when heated the salt is partially oxidized. The salt is not attacked by cold, conc. sulphuric acid, but the hot acid forms a green soln.; and with hot, conc. hydrochloric acid, chlorine is evolved.

REFERENCES.

[1] F. Wöhler, *Gött. Nachr.*, 147, 1859; A. Geuther and V. Merz, *Liebig's Ann.*, **118**. 62, 1861; O. Popp, *ib.*, **156**. 93, 1870; A. Simon, *Oesterr. Chem. Ztg.*, **28**. 195, 1925; A. Simon and T. Schmidt, *Zeit. anorg. Chem.*, **152**. 191, 1924; T. Schmidt, *Zur Kenntnis der Oxyde*, Stuttgart,

1924; E. Kopp, *Chem. News*, **11**. 16, 1864; E. Wedekind and K. Fetzer, *Ber.*, **40**. 401, 1907; E. Wedekind and C. Horst, *ib.*, **48**. 105, 1915; I. Schukoff, *Journ. Russ. Phys. Chem. Soc.*, **41**. 302, 1909; *Compt. Rend.*, **146**. 1396, 1908; L. Blanc, *Ann. Chim. Phys.*, (10), **6**. 182, 1926; L. Blanc and G. Chaudron, *Compt. Rend.*, **182**. 386, 1926; L. Blanc, *Bull. Soc. Chim.*, (4), **39**. 718, 1926; K. Honda, *Science Rep. Tohoku Univ.*, **4**. 97, 1915; K. Honda and T. Sone, *ib.*, **3**. 223, 1914.

[2] M. Traube, *Liebig's Ann.*, **66**. 87, 1848; C. F. Rammelsberg, *Pogg. Ann.*, **68**. 274, 1846; C. W. Eliot and F. H. Storer, *Proc. Amer. Acad.*, **5**. 207, 1862; *Chem. News*, **6**. 121, 136, 145, 157, 169, 182, 207, 217, 1862; A. Simon, *Oesterr. Chem. Ztg.*, **28**. 195, 1925; A. Simon and T. Schmidt, *Zeit. anorg. Chem.*, **153**. 191, 1924; T. Schmidt, *Zur Kenntnis der Oxyde*, Stuttgart, 1924.

[3] H. Löwel, *Journ. Pharm. Chim.*, (3), **7**. 321, 401, 424, 1845; A. Dalzell, *B.A. Rep.*, 68, 1859; L. N. Vauquelin, *Ann. Chim. Phys.*, (1), **25**. 21, 194, 1798; (2), **70**. 70, 1809; F. Brandenburg, *Schweigger's Journ.*, **13**. 274, 1815; *Scherer's Nord. Blatt.*, **1**. 190, 1817; *Scherer's Ann.*, **1**. 297, 1819; **2**. 126, 325, 1919; **3**. 61, 325, 1820; **4**. 187, 1820; J. W. Döbereiner, *Schweigger's Journ.*, **22**. 476, 1818; J. F. John, *ib.*, **3**. 378, 1811; H. Moser, *ib.*, **42**. 99, 1824; *Chemische Abhandlung über das Chrom*, Wien, 1824; A. Maus, *Pogg. Ann.*, **9**. 127, 1827; M. Krüger, *ib.*, **61**. 219, 1844; A. Bensch, *ib.*, **55**. 98, 1842; E. Hintz, *Liebig's Ann.*, **169**. 368, 1873; O. Popp, *ib.*, **156**. 90, 1870; H. Schiff, *ib.*, **120**. 207, 1861; **171**. 116, 1874; M. Siewert, *Zeit. ges. Naturwiss.*, **18**. 287, 1861; J. W. Swan, *Photograph. Arch.*, **11**. 301, 1870; *Dingler's Journ.*, **199**. 130, 1871; *Phot. Arch.*, **11**. 301, 1870; M. Z. Jovitschitsch, *Helvetica Chim. Acta*, **3**. 40, 1920; M. Martinon, *Bull. Soc. Chim.*, (2), **45**, 864, 1886; L. Godefroy, *ib.*, (2), **40**. 168, 1883; E. Maumené, *ib.*, (3), **7**. 174, 1892; P. Grouvelle, *Ann. Chim. Phys.*, (2), **17**. 349, 1821; L. Blanc, *ib.*, (10), **6**. 182, 1926; H. Moissan, *ib.*, (5), **21**. 243, 1880; *Compt. Rend.*, **90**. 1359, 1880; P. A. Meerburg, *Zeit. anorg. Chem.*, **54**. 31, 1907; R. Luther and T. F. Rutter, *ib.*, **54**. 29, 1907; K. Seubert and J. Carstens, *ib.*, **50**. 66, 1906; W. Manchot, *ib.*, **27**. 420, 1901; *Liebig's Ann.*, **325**. 93, 1902; W. Manchot and R. Kraus, *Ber.*, **39**. 3512, 1906; R. Kraus, *Untersuchungen über die Verbindungen von Chrom und Uran mit mehrwertigen Elementen*, Würzburg, 1906; A. Vogel, *Journ. prakt. Chem.*, (1), **77**. 482, 1859; E. Schweitzer, *ib.*, (1), **39**. 269, 1846; T. E. Thorpe, *Journ. Chem. Soc.*, **23**. 32, 1870; E. Kopp, *Chem. News*, **11**. 16, 1864; G. N. Ridley, *ib.*, **129**. 35, 1924; C. W. Eliot and F. H. Storer, *ib.*, **6**. 121, 136, 145, 157, 169, 182, 207, 217, 1862; *Proc. Amer. Acad.*, **5**. 207, 1862; W. L. Miller, *Journ. Phys. Chem.*, **11**. 9, 1907; W. M. Horton, *Proc. Chem. Soc.*, **24**. 27, 1908; S. M. Godon de St. Menin, *Ann. Chim. Phys.*, (1), **53**. 222, 1805; *Ann. Musée Hist. Nat.*, **4**. 238, 1804; *Phil. Mag.*, **20**. 266, 1805; J. J. Berzelius, *Ann. Phil.*, **3**. 104, 1814; *Schweigger's Journ.*, **22**. 56, 1818; T. Thomsen, *Phil. Trans.*, **117**. 206, 1827; L. and P. Wöhler, *Zeit. phys. Chem.*, **62**. 440, 1908; E. Moles and F. Gonzalez, *Anal. Fis. Quim.*, **21**. 204, 1923; A. Simon, *Oesterr. Chem. Ztg.*, **28**. 195, 1925; A. Simon and T. Schmidt, *Zeit. anorg. Chem.*, **153**. 191, 1924; T. Schmidt, *Zur Kenntnis der Oxyde*, Stuttgart, 1924.

[4] C. D. Braun, *Journ. prakt. Chem.*, (1), **90**. 356, 1863; J. W. Döbereiner, *Schweigger's Journ.*, **22**. 476, 1818; M. Traube, *Liebig's Ann.*, **66**. 87, 1848; K. Honda, *Science Rep. Tohoku Univ.*, **4**. 97, 1915; K. Honda and T. Ishiwara, *ib.*, **3**. 276, 1914; K. Honda and T. Sone, *ib.*, **3**. 263, 1914; C. W. Eliot and F. H. Storer, *Proc. Amer. Acad.*, **5**. 207, 1862; *Chem. News*, **6**. 121, 136, 145, 157, 169, 182, 207, 217, 1862; G. Rothaug, *Zeit. anorg. Chem.*, **84**. 165, 1913; A. Maus, *Pogg. Ann.*, **9**. 127, 1827; I. Schukoff, *Journ. Russ. Phys. Chem. Soc.*, **41**. 302, 1909; *Compt. Rend.*, **146**. 1396, 1908; A. Simon, *Oesterr. Chem. Ztg.*, **28**. 195, 1925; A. Simon and T. Schmidt, *Zeit. anorg. Chem.*, **153**. 191, 1924; T. Schmidt, *Zur Kenntnis der Oxyde*, Stuttgart, 1924; A. A. Hayes, *Amer. Journ. Science*, (1), **14**. 136, 1928; (1), **20**. 409, 1831; S. Takegami, *Bull. Japan. Chem. Soc.*, **4**. 156, 1929; E. Müller and P. Ekwall, *Zeit. Elektrochem.*, **35**. 84, 1929; E. Müller and J. Scherbakoff, *ib.*, **35**. 222, 1929.

[5] J. Heintze, *Journ. prakt. Chem.*, (2), **4**. 212, 1871; A. Leist, *ib.*, (2), **5**. 332, 1871; A. Werner and A. Klein, *Zeit. anorg. Chem.*, **9**. 294, 1895; D. Tommasi, *Bull. Soc. Chim.*, (2), **17**. 396, 1872.

§ 13. Chromium Trioxide, and Chromic Acid

The oxidation of chromic oxide, or hydrated chromic oxide furnishes **chromium trioxide,** or **chromic anhydride,** CrO_3; it was discovered by A. Mussin-Puschkin,[1] and afterwards investigated by L. N. Vauquelin, H. Moser, and J. B. Richter. Chromic oxide is oxidized to chromium trioxide, as previously indicated, by heating it in the presence of bases in air. J. Milbauer found that with oxygen at 12 atm. press., and 300°, only a partial conversion of chromic oxide to chromium trioxide occurs; and the conversion is complete at 460° and 12 atm. press. in the presence of the oxides of silver, magnesium, zinc, cadmium, and lead. The oxidation occurs more readily than with oxygen if chromic oxide be heated with oxidizing agents—*e.g.* alkali nitrate, chlorate, dioxide, etc. A. Mailfert found that ozone converts chromic hydroxide into chromium trioxide. In alkaline soln., chromic oxide or hydroxide is oxidized to the trioxide by chlorine or hypochlorite (A. J. Balard,

H. Vohl), fluorine (F. Fichter and E. Brunner), bromine (F. H. Storer, F. Melde), iodine (E. Lenssen), hydrogen dioxide or alkali dioxide (E. Lenssen), potassium persulphate (H. Marshall, and D. M. Yost), potassium ferricyanide (E. Lenssen), potassium permanganate (A. Reynoso, S. Cloez and E. Guignet, and E. Bohlig), perchloric acid (J. J. Lichtin), lead dioxide (G. Chancel), manganese dioxide (F. H. Storer), mercuric oxide (F. H. Storer), copper oxide (O. W. Gibbs), and silver oxide (D. Meneghini). In acidic soln., according to F. H. Storer, A. Terni, and M. Salinger, chromic oxide is oxidized by potassium permanganate, or by lead or manganese dioxide; and, according to M. Holzmann, by ceric nitrate. O. Stumm found that chromic salts in alkaline soln. can be oxidized by molecular oxygen, using manganese hydroxide, copper hydroxide, cerium hydroxide, silver oxide and iodide, and amalgamated copper as catalytic agents. For the electrolytic oxidation, *vide supra*, the extraction of chromium.

K. Fischbeck and E. Einecke found that the cathodic polarization of ferrous, cuprous, calcium, and magnesium chromites produces chromic acid, whilst the other chromites are unaffected, and natural chrome ironstone behaves in a like manner, but other commercial chromites are reduced on cathodic polarization, and yield chromic acid on anodic polarization. Chromites behave as an intermediate electrode. O. Unverdorben observed that chromyl fluoride, prepared by heating a mixture of fluorspar, lead chromate, and sulphuric acid, when passed into water, furnishes an aq. soln. of this oxide. The soln. was treated with silver nitrate, and the washed precipitate of silver chromate decomposed by hydrochloric acid. A. Maus said that anhydrous sulphuric acid or fuming sulphuric acid is not suited for the preparation because of its volatilization with the chromyl fluoride. J. J. Berzelius employed a somewhat similar process using either lead or barium chromate. A. Maus treated a hot soln. of potassium dichromate with insufficient hydrofluosilicic acid to precipitate all the potassium; the filtered soln. was evaporated and again treated with hydrofluosilicic acid, and evaporated to dryness in a platinum dish. The residue was taken up with a little water, filtered, and evaporated for chromic anhydride. D. G. Fitzgerald and B. C. Molloy precipitated the potassium as potash-alum by adding aluminium sulphate, and removed the sulphuric acid by ignition. J. Fritzsche added a warm soln. of potassium dichromate to an excess of conc. sulphuric acid; the chromic anhydride separates in small red crystals. The liquid is drained from the crystals, which are then dried on a porous tile over sulphuric acid. The crystals are then recrystallized from an aq. soln. P. A. Bolley said that the chromic anhydride so prepared contains a little sulphuric acid as impurity and the Metals Protection Corporation removed the sulphate by means of barium hydroxide, carbonate, or chromate. R. Bunsen, A. V. Rakowsky, A. Dalzell, F. Dietze, O. Ficinus, H. Moissan, A. Schafarik, M. Traube, J. Voisin, G. Vulpius, R. Warington, and E. Zettnow employed modifications of these processes.

G. P. Baxter and co-workers purified chromium trioxide suitable for at. wt. determinations by repeated filtration, and recrystallization from aq. soln. M. Siewert treated barium chromate with nitric acid, crystallized out the barium nitrate; removed the nitric acid by evaporation to dryness; and recrystallized the product. E. Duvillier used a similar process, and afterwards substituted lead chromate for barium chromate. K. F. W. Meissner, F. Kuhlmann, J. W. Döbereiner, and W. A. Rowell treated barium chromate with sulphuric acid; and A. Schrötter, lead chromate. The filtered liquid in each case was evaporated for crystallization. J. Thomsen, and J. Krutwig similarly treated silver chromate with hydrochloric acid. A. Mailfert found that chromium trioxide is formed when soln. of chromic salts or chromic oxide are treated with ozone. M. Prud'homme and F. Binder observed that if barium chloride is added to a soln. of barium dichromate, normal barium chromate is precipitated, and potassium chloride and chromic acid remain in soln. In preparing chromic acid, V. V. Polyansky first obtained calcium chromate by addition of calcium hydroxide paste, followed by calcium chloride soln., to aqueous sodium dichromate ; the mixture is concentrated on the water-bath, the precipitate of calcium chromate being collected and dried. Two parts of the aq. soln. is treated with one part of sulphuric acid (sp. gr. 1·84), kept on the water-bath, decanted, and this procedure repeated until no more calcium sulphate is precipitated, when chromic anhydride is crystallized. The product is treated with nitric acid (sp. gr. 1·4), and dried at 60°–100°.

For the electrolytic oxidation of soln. of chromic salts to chromic acid or the chromates, *vide supra.* According to E. Müller and M. Soller, a soln. of chrome-alum in N-H_2SO_4 is not appreciably oxidized to chromic acid with a smooth platinum anode, but when traces of a lead salt are present in the soln., lead dioxide is deposited on the anode, and oxidation then occurs. About one-third of the oxidation which occurs with a lead dioxide anode occurs when an anode of platinized platinum is used. With a lead dioxide anode, the oxidation occurs quantitatively in fairly conc. soln. of chrome-alum, when the current density is not too high—about 0·005 amp. per sq. cm. is suitable. The difference in the results is not due to the lead dioxide anode having a higher potential than the platinum anode, since the reverse is rather the case. The effect is attributed to the catalytic action of lead dioxide which oxidizes the chrome-alum chemically. P. Askenasy and A. Révai showed that in regenerating soln. of chromic sulphate, at first, when the conc. of the chromic acid is small, it is better to use low-current densities at the cathode, and to increase the current density as the conc. of chromic acid increases. Temp. has little influence on the process. The addition of magnesium sulphate prevents a reduction at the cathode when dil. soln. and low current densities are employed, but if there is only a small percentage of chromic acid present it has the opposite effect, and if high current densities are used, it has no effect. The influence of chromium sulphate is to prevent reduction with both high and low-current densities except in soln. which contain very little chromic acid. The addition of sodium and potassium sulphates is without influence on the reaction. Dilution is favourable to the oxidation under all circumstances, but more especially with high-current densities and in the presence of magnesium sulphate when low-current densities are employed. A high conc. of sulphuric acid has a slightly favourable action. A. R. y Miro found that the presence of potassium fluoride favours the electrolytic oxidation of chrome-alum to potassium dichromate.

It is doubtful if hydrated chromium trioxide has been prepared in the solid state. H. Moissan[2] said that if an almost sat. aq. soln. of chromium trioxide be kept for several hrs. at about 90°, and then cooled below 0°, small red crystals of **chromic acid,** H_2CrO_4, collect on the walls of the containing vessel. This does not agree with J. J. Berzelius's observations, while F. Mylius and R. Funk, T. Costa, and E. Field were unable to confirm H. Moissan's observation. H. C. Jones showed that the f.p. of aq. soln. of chromium trioxide agreed with the assumption that the solvation for soln. with m mols of CrO_3 per litre, can be represented by the mols of water in combination with a mol of CrO_3 :

Mols CrO_3 per litre .	0·10	0·50	1·00	2·00	3·00	4·00
Mols H_2O per mol CrO_3 .	27·8	20·6	19·17	13·95	11·65	10·41

The crystals are chromium trioxide, CrO_3, not chromic acid, H_2CrO_4. The **solubility** of chromium trioxide in water was measured by R. Kremann who found that sat. soln. at $\theta°$ contained S grms. of CrO_3 per 100 grms. of soln.

	−74·0°	−64·0°	−52·0°	−43·0°	−28·3°	−16·3°	−2·0°
S	55·00	54·00	52·00	49·10	40·80	30·20	8·00

There is a eutectic at —105° with 57·2 per cent. of CrO_3. E. H. Büchner and A. Prins gave —155·0° for the eutectic with 60·5 per cent. of CrO_3. At higher temp. J. Koppel and R. Blumenthal, F. Mylius and R. Funk, and R. Kremann found :

	0°	15°	30°	50°	82°	100·0°	127·0°
S	61·82	62·40	62·52	64·60	66·00	67·40	71·20

The results of E. H. Büchner and A. Prins are plotted in Fig. 24 ; there is no sign of the formation of a definite hydrate. C. F. Hüttig and B. Kurre also failed to find any evidence of the formation of any definite hydrate. Analyses of chromium trioxide by L. N. Vauquelin, S. M. Godon de St. Menin, C. F. Rammelsberg, J. J. Berzelius, and A. Schrötter are in agreement with the empirical formula CrO_3. W. Ostwald's observations on the electrical conductivity, and the lowering of the f.p. indicate that the **molecular weight** in aq. soln. of chromium trioxide corresponds with **dichromic acid,** $H_2Cr_2O_7$; and this is in agreement with a comparison of the absorption spectra of aq. soln. of chromium trioxide and potassium dichromate, for H. Settegast found these spectra are very much alike. According to R. Abegg and A. J. Cox, the electrical conductivity and f.p. of soln. of the dichromates agree with the assumption that dichromic acid, $H_2Cr_2O_7$, chromic acid, H_2CrO_4, and chromium trioxide are present. E. Spitalsky, however, interpreted the results of his observations on the ionization of the aq. soln. to mean that the soln. is ionized $H_2Cr_2O_7 \rightleftharpoons 2H^{\cdot} + Cr_2O_7{}''$. The resolution of the dichromate into chromate ions was not observed with a mol of CrO_3 in 5800 litres. E. Field's observations on the raising of the b.p. of aq. soln. indicate a mol. wt. of 171·85 when H_2CrO_4 requires 118·4, and $H_2Cr_2O_7$ requires 218·8. T. Costa's ebulliscopic measurements show that soln. which are not too concentrated, at 100° contain $H_2Cr_2O_7$, not H_2CrO_4 ; and that a soln. of chromic acid has the same electrical conductivity when cooled to 0° either directly or after heating to 100°, so that no chromic acid, H_2CrO_4, is formed in soln. K. Seubert and J. Carstens explained the action of hydrazine on the assumption that the soln. contained $H_2Cr_2O_7$, or $Cr_2O_7{}''$-ions. M. S. Sherrill found that the f.p. of soln. of ammonium chromate agreed with the assumption that $HCrO_4{}'$-ions are present. W. V. Bhagwat and N. R. Dhar, N. R. Dhar, and F. Auerbach assumed the existence of H_2CrO_4 in aq. soln. H. Lessheim and co-workers, and P. Niggli discussed the electronic structure.

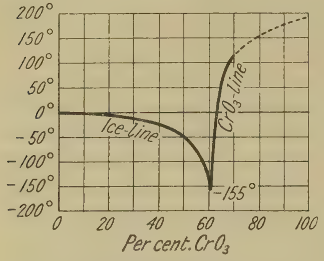
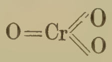
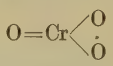


FIG. 24.—Solubility Curve of Chromium Trioxide.

The generally accepted view—*vide supra*—is that chromium is sexivalent in the trioxide ; but W. Manchot supposed that it is quadrivalent :

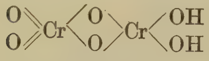


Sexivalent Cr

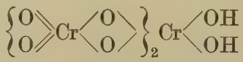


Quadrivalent Cr

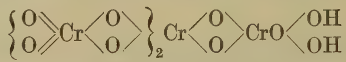
he supported this hypothesis by comparing the reactions of the trioxide with those of the peroxides, but R. Luther and T. F. Rutter did not agree. A. Geuther supposed that the polychromates are salts of hypothetical polychromic acids :



Dichromic acid.

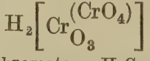


Trichromic acid.



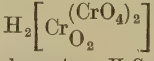
Tetrachromic acid.

A. Miolati represented chromic acid on the co-ordination theory by $H_2[CrO_4]$, and the polychromic acids by $H_2[Cr(CrO_4)O_3]$, in which the oxygen atoms of the O_3-group are replaced by CrO_4-radicles :



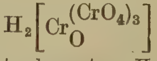
$$H_2\left[Cr^{(CrO_4)}_{O_3}\right]$$

Dichromate, $-H_2Cr_2O_7$.



$$H_2\left[Cr^{(CrO_4)_2}_{O_2}\right]$$

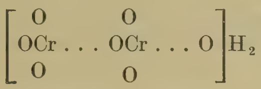
Trichromate, $-H_2Cr_3O_{10}$.



$$H_2\left[Cr^{(CrO_4)_3}_{O}\right]$$

Tetrachromate, $-H_2Cr_4O_{13}$.

In addition to a number of inorganic polychromates, R. Weinland and H. Staelin prepared dichromates of quinoline and guanidine ; and trichromates of quinoline, pyridine and guanidine. A. Werner represented dichromic acid as a derivative of dimolecular chromium trioxide $(CrO_3)_2$, and on his co-ordination theory, dichromic acid becomes:



$$\left[\begin{matrix} O & & O & & \\ OCr & \ldots & OCr & \ldots & O \\ O & & O & & \end{matrix}\right]H_2$$

The physical properties of chromium trioxide.—The evaporation of the aq. soln. of chromium trioxide furnishes a dark red mass. The colour was found by F. Rinne [3] to darken with a rise of temp., and to be restored on cooling. When the trioxide is crystallized in the presence of sulphuric acid, dark red, needle-like **crystals** are formed, which, according to A. E. Nordenskjöld, are rhombic bipyramids with the axial ratios $a:b:c=0·692:1:0·628$. The fused trioxide furnishes a hard, brittle, coral-red, crystalline mass, which forms a scarlet-red powder. L. Playfair and J. P. Joule gave 2·676 for the **specific gravity** of the crystallized trioxide; C. H. D. Bödeker gave 2·737 at 14°, and for that which had been fused, 2·629 at 14°, while A. Schafarik gave 2·819 at 20°; W. A. Roth and G. Becker, 2·80 at 21°; and E. Zettnow, 2·775 to 2·804. H. C. Jones and H. P. Bassett measured the sp. gr. of soln. with from 0·10 to 4·00 mols of CrO_3 per litre with the idea of calculating the solvation of chromium trioxide in soln.—*vide supra.* The sp. gr. of aq. soln. of the trioxide were determined by D. J. Mendeléeff, and E. Zettnow; the following are averages of the two sets of observations, at 15°:

CrO_3 .	5	10	15	20	30	40	50	60 per cent.
Sp. gr. .	1·0365	1·0760	1·1185	1·1640	1·2630	1·3780	1·5110	1·656

H. R. Moore and W. Blum found the sp. gr. at 25° of soln. of chromic acid containing at 25°, C mols of CrO_3 per litre:

C . .	1	2	3	4	5	6	7	8	9	10
Sp. gr. .	1·0125	1·1383	1·2041	1·2699	1·3358	1·4016	1·4674	1·5332	1·5990	1·6648

W. Biltz discussed the mol. vol.; and C. del Fresno, the contraction in vol. which occurs when the compound is formed. The **viscosity,** η (water unity) dynes per cm. for aq. soln. of chromium trioxide containing ω grm. CrO_3 per 100 grms. of water, is:

0°	ω . . .	111·4	72·86	51·38	29·59
	η . . .	1·482	1·195	1·110	1·057
18°	ω . . .	98·8	71·01	35·92	16·71
	η . . .	1·5116	1·2849	1·1017	1·0349
25°	ω . . .	147·4	89·40	42·68	12·05
	η . . .	2·3360	1·4880	1·1360	1·024
40°	ω . . .	111·4	72·86	51·38	16·55
	η . . .	1·328	1·164	1·1055	1·027

S. A. Mumford and L. F. Gilbert found the sp. gr. of soln. of chromic acid containing M mols per litre at 25°/4°, to be:

M . . .	10·713	7·288	5·176	2·322	0·842	0·206	0·060	0·013
Sp. gr. . .	1·7042	1·4835	1·3479	1·1530	1·0602	1·0119	1·0012	0·9981

and at 45°/4°:

M . .	10·768	7·034	5·890	2·829	2·069	1·082	0·459	0·226
Sp. gr. . .	1·6954	1·4593	1·3813	1·1831	1·1306	1·0599	1·0226	1·0063

G. G. and I. N. Longinescu calculated the sp. gr. of the soln. considered as a binary mixture. C. del Fresno, and D. Balareff studied the mol. vol. R. Dubrisay measured the **surface tension** during the progressive neutralization of chromic acid soln. by soln. of sodium hydroxide, and by ammonia, and found that chromic acid differs from a strong dibasic acid, such as sulphuric acid, in exhibiting a constant surface tension only until the first acid function is neutralized, after which the surface tension decreases gradually but slightly until the second is neutralized, when, as usual, a great decrease occurs. T. Graham made observations on the rate of **diffusion** of chromium trioxide in aq. soln.

The **specific heat** of aq. soln. of chromium trioxide, between 21° and 53°, was measured by J. C. G. de Marignac.[4] E. H. Buchner and A. Prins gave for soln. with the molar ratio $CrO_3 : nH_2O$:

n	3·55	5·02	9·91	25·2	50	87·9	100·5	200
Sp. ht.	0·506	0·557	0·665	0·803	0·876	0·927	0·942	0·970

The last two sets of data are by J. C. G. de Marignac. The subject was discussed by N. de Kolossowsky. O. Unverdorben, J. J. Berzelius, H. Moissan, E. Hintz, and A. Schafarik observed that when chromium trioxide is heated, it becomes almost black and then melts to a reddish-brown liquid. M. Traube gave 180°–190° for the **melting point ;** F. M. Jäger and H. C. Germs, 198° ; and E. Groschuff said that the trioxide melts at 196° with a little decomposition, and that the molten mass can be easily under-cooled 26° ; E. Zettnow gave 170°–172° for the f.p., and said that on solidification, the temp. may rise to 193° ; and that there is a large contraction on solidification. The **freezing points** of aq. soln. of chromium trioxide are indicated in Fig. 24. J. Koppel and R. Blumenthal gave :

CrO_3	23·1	28·6	44·4	50·0	54·5 per cent.
Freezing point	−6°	−9·3°	−24°	−36°	−51°

and W. Ostwald, and R. Abegg and A. J. Cox made observations on the mol. lowering of the f.p. of aq. soln. H. C. Jones and H. P. Bassett found that with soln. containing m mol of CrO_3 per litre, the lowering of the f.p. was :

m	0·10	1·0	2·5	4·00
Fall of f.p.	5·26°	6·78°	9·00°	14·40°

E. Cornec measured the lowering of the f.p. of aq. soln. of chromic acid during its progressive neutralization with sodium hydroxide. There is a break in the curve corresponding with the formation of the dichromate, and another break corresponding with the chromate. J. J. Berzelius, A. Schafarik, H. Moissan, and E. Hintz noticed that when heated to near the b.p. of sulphuric acid, chromium trioxide **volatilizes** forming reddish fumes. O. Unverdorben, A. Schafarik, and J. J. Berzelius observed that chromium trioxide decomposes above its m.p. into oxygen and chromic oxide with a glow, but if the chromium trioxide has been obtained by evaporation no glowing occurs. H. Arctowsky said that decomposition occurs at 200° ; and I. Schukoff added that the trioxide decomposes with deflagration at 300°, with the evolution of oxygen. L. and P. Wöhler said that below 1200°, the reaction $2CrO_3 = Cr_2O_3 + 3O$ is not reversible and is probably exothermal ; but in the presence of potassium sulphate, at 1000°, the reaction, $2K_2SO_4 + Cr_2O_3 + 3O \rightleftharpoons 2(K_2SO_4.CrO_3)$, is reversible, and at 1009°, the press. of the oxygen is 878 mm. ; at 1029°, 785 mm. A. Simon and T. Schmidt's heating curve, and dissociation press. curve are shown in Fig. 22. K. S. Nargund and H. E. Watson found that 2 hrs.' heating at 300° resulted in a 28 per cent. decomposition ; at 350°, 48 per cent. ; at 400°, 52 per cent. ; at 550°, 100 per cent. ; 9 hrs. at 350°, 52 per cent., and 18 hrs. at 350°, 55 per cent. R. Read observed that in the non-luminous flame chromium trioxide decomposes with a bright, white incandescence. H. Arctowsky noticed that when heated to 125°, under 16 mm. press., chromium trioxide volatilizes forming a sublimate of long, red needles. J. Koppel and R. Blumenthal observed the **boiling points** of aq. soln. of chromium trioxide, at ordinary press. :

CrO_3	10·81	24·08	45·15	61·54	71·24 per cent.
Boiling point	102°	102°	110·5°	120°	127°

and T. Costa found the mol. rise of the b.p. of aq. soln. to be :

CrO_3	1·5233	1·7886	3·8212	11·5159 per cent.
Rise of temp.	15·6°	14·3°	14·1°	13·7°

Observations were also made by E. Field—*vide supra.* W. G. Mixter gave for the **heat of formation** of chromium trioxide, CrO_3, from its elements, 140 Cals.; amorphous chromic oxide, 36·2 Cals.; and from crystalline chromic oxide 26·1 Cals., whilst M. Berthelot gave 26·2 Cals. W. A. Roth and G. Becker gave $(Cr,\frac{3}{2}O_2)=147{\cdot}1$ Cals.; and for the heat of reduction of CrO_3 to Cr_2O_3, $-6{\cdot}1$ Cals. J. Thomsen gave for the heat of formation in aq. soln., 18·913 Cals., and M. Berthelot, 10·6 Cals. The subject was discussed by A. Berkenheim. According to F. Morges, the heat of solution of CrO_3 in water is $CrO_3+H_2O=H_2CrO_4+580$ cals.; for $H_2CrO_4+H_2O$, 340 cals.; for $H_2CrO_4.H_2O+H_2O=260$ cals.; for $H_2CrO_4.2H_2O+H_2O$, 135 cals.; $H_2CrO_4.3H_2O+H_2O$, 171 cals.; $H_2CrO_4.4H_2O+H_2O$, 80 cals.; $H_2CrO_4.5H_2O+H_2O$, 35 cals.; $H_2CrO_4.5H_2O+25H_2O$, 500 cals.; and $H_2CrO_4.30H_2O+25H_2O$, 210 cals. P. Sabatier gave 1·9 cals. for the heat of soln. in 40 times its weight of water at 19°. E. H. Büchner and A. Prins gave for the **heat of dilution** from $CrO_3.nH_2O$ to $CrO_3.80H_2O$, and the total heat of soln. when the heat of soln. for a mol of solid CrO_3 and 80 mols of water is 24·67 cals.:

n	3·32	4·03	4·96	10·1	25·2	49·9
Heat dilution	1447	1111	866	469	122	16
Heat solution	1020	1356	1601	1998	2345	2451

J. Thomsen gave for the **heat of neutralization,** $(CrO_3,NaOH_{aq.})=13{\cdot}134$ Cals.; for $(CrO_3,2NaOH_{aq.})=24{\cdot}720$ Cals.; P. Sabatier gave $(2CrO_3,K_2O_{aq.})=27{\cdot}0$ Cals.; $(2CrO_3,2K_2O_{aq.})=50{\cdot}8$ Cals.; while M. Berthelot gave $(2CrO_3,K_2O_{aq.})=26{\cdot}8$ Cals.; $(2CrO_3,2NH_{3aq.})=24{\cdot}0$ Cals.; for solid chromium trioxide, $(CrO_3,K_2O)=95{\cdot}6$ Cals.; $(2CrO_3.K_2O)=106{\cdot}8$ Cals., when for solids $(SO_3,K_2O)=141{\cdot}4$ Cals., and $(2SO_3,K_2O)=167{\cdot}6$ Cals.

E. Cornec measured the **index of refraction** of a soln. of chromic acid during its progressive neutralization with potassium hydroxide and with aq. ammonia. The results show that the aq. soln. of the acid first furnishes dichromate, and as the proportion of base increases, chromate is formed. W. J. Pope[5] gave 37·13 for the refraction equivalent of the CrO_4-radicle. J. Piccard and E. Thomas discussed the colour of chromate and dichromate ions. The **absorption spectrum** of aq. soln. of chromium trioxide was examined by J. H. Gladstone.[6] J. M. Hiebendaal showed that the green and blue rays are absorbed by the soln. According to A. Étard, there is a fine absorption band between $\lambda=6870$ and 6800 with conc. soln.; but soln. of potassium chromate and dichromate do not show this band. H. Settegast measured the absorption spectrum; and P. Sabatier found that the coeff. of absorption, a, for light of different wave-lengths, λ, is not sensibly affected by the thickness, λ, of the layer of liquid through which the light is passed. Here, $l=l_0 10^{-a\lambda}$ with light of intensity l_0:

λ	5450	5480	5550	5620	5690	5770	5850	5930
a	0·005	0·025	0·143	0·351	0·628	0·812	0·900	0·950

Beyond wave-length 5450 the coeff. becomes practically zero; in very dil. soln., the coeff. for wave-length 5180 is about 0·000013. The values are the same for the acid as for the salts, for solid potassium dichromate as for its soln., for the ammonium salt as for the potassium salt, and it follows that the absorption exerted by solid or dissolved alkaline dichromates is sensibly identical with that of the chromic acid which they contain. With soln. of potassium chromate, the absorption is in the blue and the violet, and with dilution, the absorption extends more in the direction of the red. Thus, O. Knoblauch found that in conc. soln., the absorption begins at 4900, and in dil. soln., at 5100. W. Böhlendorff obtained similar results; while J. M. Hiebendaal observed that the absorption begins at 5050, and in dil. soln. at 4770. K. Vierordt, P. Pogany, F. Grünbaum, A. Hantzsch, P. Bovis, N. R. Tawde and G. R. Paranjpe, G. Jander and T. Aden, M. N. Saha, C. P. Snow and F. I. G. Rawlins, and H. Settegast made observations on this subject; and P. Sabatier found that with potassium chromate soln., the coeff. of transmission, a, for soln. with one eq. of salt per litre, and, α_2, for soln. with 2 eq. per litre, were:

λ .	4940	4990	5030	5060	5080	5110	5130	5180	5240
α_1 .	—	0·06	0·18	0·325	0·44	0·61	0·69	0·85	0·92
α_2 .	0·025	0·108	0·207	0·43	0·51	0·62	0·69	0·84	0·93

The absorption is slightly greater in the more dil. soln., and this points to slight dissociation with formation of some dichromate, which, however, is only produced in very minute quantity. H. Becquerel found that soln. of potassim chromate are transparent for the ultra-red rays; and G. Massol and A. Faucon studied the transmission of ultra-violet rays. D. Brewster investigated the absorption spectrum of soln. of ammonium chromate; and J. H. Gladstone, soln. of metal chromates. H. von Halban and H. Siedentopf found that a soln. of potassium chromate in $0·05N$-KOH had the extinction coeff., ϵ, for light of wave-length, λ, when $I=I_0 10^{-\epsilon Cd}$, where C denotes the conc. in mols per litre.

λ .	2540	2650	2970	3130	3340	2800	2890	3600	4360
$\epsilon \times 10^{-3}$	2·35	3·00	0·927	0·1935	0·9850	3·290	2·086	4·416	0·3138

H. C. Jones and W. W. Strong found that the absorption spectra of conc. soln. of potassium chromate shows a stronger absorption than the value calculated from Beer's law. G. Rudorf discussed the applicability of Beer's law. F. Weigert, and H. von Halban and H. Siedentopf studied the absorption of light by mixed soln. of potassium chromate and copper sulphate. Observations on the absorption spectrum of soln. of potassium dichromate were made by H. Bremer, P. Glan, F. Grünbaum, H. C. Jones and W. W. Strong, B. K. Mukerji and co-workers, F. Melde, J. Müller, P. Pogány, P. Sabatier, H. Settegast, C. P. Smyth, G. Jander and T. Aden, and K. Vierordt. According to J. Formanek, aq. soln. of potassium dichromate absorb the blue and violet rays, and with decreasing concentration, the absorption extends in the direction of the red rays. O. Knoblauch found that with conc. soln., the absorption begins at 5200, and is complete at 4940, while with dil. soln., absorption begins at 5070, and is complete at 4840. W. Böhlendorff gave for the limit 5000, and J. M. Hiebendaal, 5250. A. Hantzsch's observations are summarized in Fig. 25. G. Hantzsch and R. H. Clark found that soln. of chromium trioxide in water and in aq. sulphuric acid are at all conc. optically identical with each other and with feebly acidic soln. of potassium dichromate. Soln. of the latter in water deviate very slightly in the direction of monochromate soln. Soln. of monochromates in water, in alkalis, and in methyl alcohol, are at all conc. quite different from dichromate and chromic acid soln. in their optical characteristics, but are identical among themselves, except for a slight deviation of the aq. soln. in the direction of the dichromate soln. The optical characteristics are independent, not only of the conc. and the solvent, but also of the temp. The chromophoric group in all acidic soln. is the completely saturated complex Cr_2O_7; in all alkaline soln. the corresponding complex is CrO_4. From the optical point of view, it is immaterial whether these complexes are combined with hydrogen or alkali metal, ionized or non-ionized; the colour of the ions must be the same as that of the non-ionized molecule. A. Hantzsch and C. S. Garrett explain the slight divergence from Beer's law with very conc., alkaline soln. of chromates by incomplete hydration rather than by ionization changes. All variations from the colorimetric law are attributed either to experimental errors, or to chemical changes between solvent and solute. H. M. Vernon estimated the degree of ionization from the colour

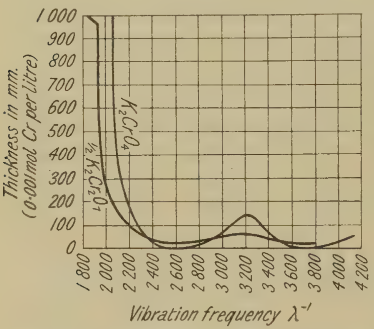


Fig. 25.—Absorption Spectra of Chromate Solutions.

of aq.soln. of the trioxide. E. Viterbi and G. Krausz measured the absorption spectra of soln. of chromic acid, and of potassium chromate and dichromate. There are seven feeble lines in the ultra-violet spectra of chromic acid and potassium dichromate which do not occur with soln. of the chromate. The bands with the chromate soln. are sharper than those with chromic acid or the dichromate. Except for a few minor differences, the spectra of the dichromate and of chromic acid are similar, and conform to Beer's law. Hence it is assumed that in these soln., the chromium is nearly all present as Cr_2O_7'', which has the same absorption spectrum either as an ion or as a non-ionized molecule; but probably with dil. soln. of the dichromate, there is some dissociation either as $Cr_2O_7''+H_2O\rightleftharpoons 2CrO_4''+2H^{\cdot}$, or as $Cr_2O_7''+H_2O \rightleftharpoons 2HCrO_4'$. Soln. of potassium chromate do not follow Beer's law, but the results with dil. soln. approach those with soln. of the dichromate, owing, probably, to a reaction $2CrO_4''+H_2O\rightleftharpoons Cr_2O_7''+2OH'$; and the addition of a large proportion of alkali displaces the equilibrium towards the left and restores the results for the absorption spectrum of the chromate. R. Robl observed but a faint luminescence in ultra-violet light; and A. Karl found the crystals triboluminescent. W. Spring found that there is a slight change of colour when soln. of potassium dichromate are allowed to stand. This shows that there is a change in the constitution of the soln. A. M. Taylor examined the **ultra-red spectrum**; D. M. Yost, the K-absorption spectrum; and N. Nisi, the **Raman effect**.

Both H. Buff,[7] and L. Bleekrode said that molten chromium trioxide is a good conductor of electricity, but J. W. Hittorf showed that the trioxide is a conductor only when it is contaminated with impurities, particularly water; the purified trioxide is a non-conductor. The **electrical conductivity** of aq. soln. was measured by R. Lenz, W. Ostwald, R. Abegg and A. J. Cox, E. Spitalsky, H. C. Jones and H. P. Bassett, etc. P. Walden found that with soln. containing a mol of the salt in v litres of water at 25°, the mol. conductivities, μ, are:

v	16	32	64	128	256	512	1024
μ	347·1	354·7	358·9	361·3	360·8	358·4	353·7

H. C. Jones gave for the molar conductivity, μ, at 0°, and the percentage **degree of ionization,** α,

v	0·286	0·500	1·000	2·500	5·00	10·00	20·00	40·00
μ	108·4	206·8	312·4	388·9	420·0	436·0	440·0	452·0
α	20·7	39·3	59·7	74·3	80·3	83·4	84·1	86·4

The conductivity at infinite dilution is 523. The assumption that the ionization is represented by $H_2CrO_4=H^{\cdot}+HCrO_4'=2H^{\cdot}+CrO_4''$, does not explain the facts. The nature of the molecules formed in aq. soln. depends on the composition, concentration, and temp. of the soln. This has been the subject of many investigations and the results are usually expressed in the language of the ionic hypothesis. Whatever be the equilibrium condition, that state is quickly attained; and the result was shown by K. Beck and P. Stegmüller, T. Costa, M. S. Sherrill, and P. Walden to be independent of the mode of preparation of the soln. A. Hantzsch's optical measurements show that it is very improbable that chromium trioxide exists in aq. soln. as CrO_3, or in the ionic form CrO_4'' or $HCrO_4'$. He therefore assumed that in solid, and in aq. soln., the equilibrium condition: $nCrO_3+H_2O\rightleftharpoons(CrO_3)n.H_2O$, is almost wholly in favour of the polymerized product.

With the most concentrated soln. of chromium trioxide in water, it is probable that trichromic and tetrachromic acids are formed, but in more dilute soln., only monochromic and dichromic acids are involved; the former may be ionized: $H_2CrO_4\rightleftharpoons H^{\cdot}+HCrO_4'=2H^{\cdot}+CrO_4''$, and the latter: $H_2Cr_2O_7\rightleftharpoons H^{\cdot}+HCr_2O_7' \rightleftharpoons 2H^{\cdot}+Cr_2O_7''$. It was, therefore, inferred that chromic acid, H_2CrO_4, exists in soln., and that it behaves as a monobasic acid $H(HCrO_4)$, ionizing: $H_2CrO_4 =H^{\cdot}+HCrO_4'$. R. Abegg and A. J. Cox took a similar view, and added that even with soln. of the dichromates, there is a relatively small proportion of Cr_2O_7''-ions, and that as the temp. rises, the Cr_2O_7''-ions form CrO_4''-ions and chromic acid.

E. Carrière and P. Castel studied the ionic equilibrium $2CrO_4''+2H^{\cdot}\rightleftharpoons Cr_2O_7''+H_2O$ at 20° by the conversion of barium chromate into barium dichromate by the addition of a measured amount of hydrochloric acid, the end-point being reached when the soln. becomes clear. The hydrogen-ion conc. of the equilibrium mixture was calculated from the law of mass action applied to the ions concerned assuming complete ionization, and good agreement was found between the observed and calculated values for low conc. The conc. of acid required decreases with temp., and the equilibrium constant at 18° is 3×10^{-15}. P. Walden concluded from the small change in the electrical conductivity of the soln. between the dilutions $v=32$ and $v=1024$, that a strong monobasic acid is involved and that this is almost completely ionized with the dilution $v=32$. W. Ostwald, however, concluded that the acid exists in aq. soln., not as H_2CrO_4, but as $H_2Cr_2O_7$; and in support of this he showed that an aq. soln. which contains a mol of a compound per kilogram lowers the f.p. $-1·85°$. Acetic acid gives nearly the normal value $-1·92°$; nitric acid gives $-3·70°$, nearly twice the normal value, in agreement with the assumption that it is almost completely ionized into $H^{\cdot}$ and NO_3' ions; sulphuric acid gives $-2·00°$ in agreement with the assumption that it is ionized $H_2SO_4\rightleftharpoons 2H^{\cdot}+SO_4''$ to the extent of about 0·6; and chromic acid gives $-1·34°$ in agreement with the assumption that it is completely ionized $H_2Cr_2O_7\rightleftharpoons 2H^{\cdot}+Cr_2O_7''$, and this is in accord with the observations of P. Walden. According to W. C. D. Whetham, the eq. conductivity, λ, of soln. of potassium dichromate containing m eq. per litre is:

m	0·00001	0·0001	0·001	0·01	0·1	0·2
λ	81·3	76·3	71·4	70·4	64·3	61·5

The rise of the conductivity with dilution up to $m=0·0001$ is unusually small, and this is attributed to the hydrolysis of the Cr_2O_7''-ions to the slow-moving $HCrO_4'$-ions. The unusually large rise in the conductivity when the soln. is diluted from $m=0·0001$ to $m=0·00001$, is attributed to the ionization $HCrO_4'\rightleftharpoons H^{\cdot}+CrO_4''$ or possibly $HCr_2O_7'\rightleftharpoons H^{\cdot}+Cr_2O_7''$. H. R. Moore and W. Blum found the electrical conductivity κ mhos of soln. of C mols of chromic acid per litre at 25° to be:

C		1	2	3	4	5	6	7	8	9	10
κ	0°	0·219	0·342	0·418	0·440	0·435	0·420	0·387	0·345	0·289	0·225
	25°	0·315	0·513	0·616	0·657	0·662	0·641	0·600	0·545	0·477	0·402
	45°	0·389	0·632	0·763	0·818	0·831	0·817	0·769	0·708	0·625	0·528

The resulting curves show a maximum for about $4M$-soln. at 0°; for $4·8M$-soln. at 25°; and for $5·0M$-soln. at 45°. This shift is greater than can be explained by the change in sp. gr. or in vol. conc. caused by the difference in temp.; it must therefore involve a difference in the degree or type of dissociation of the chromic acid. R. N. J. Saal found the equilibrium constant of the reaction $Cr_2O_7''+H_2O\rightleftharpoons 2HCrO_4'$ to be 0·019. The decomposition of dichromate to chromate may occur (i) in the alkaline region: $Cr_2O_7''+OH'\rightarrow CrO_4''+HCrO_4'$; (ii) in the acidic and neutral region: $Cr_2O_7''+H_2O\rightarrow 2HCrO_4'$; and (iii) diluting the soln. with acid and water: $Cr_2O_7''+H^{\cdot}+H_2O(\rightleftharpoons HCr_2O_7'+H_2O)\rightarrow 2HCrO_4'+H^{\cdot}$. N. R. Dhar studied this subject. According to E. Spitalsky, the **hydrogen-ion concentration,** $[H^{\cdot}]$, in dil. soln. of chromic acid of [Cr], is:

[Cr]	0·002446	0·001218	0·000609	0·000602	0·000344	0·000172
$[H^{\cdot}]$	0·00249	0·00121	0·000606	0·000595	0·000342	0·000166

so that the ratio $[H^{\cdot}]:[Cr]$ is nearly unity in harmony with the assumption that with dil. soln. of chromic acid, the ionization is: $H_2CrO_4\rightleftharpoons H^{\cdot}+HCrO_4'$. The electrometric titration of chromic acid soln. was made by A. Miolati and E. Mascetti, N. H. Furman, R. N. J. Saal, Y. Kato and T. Murakami, W. S. Hughes, N. Westberg, and L. Margaillan. H. T. S. Britton obtained the results summarized in Fig. 26, by means of the hydrogen electrode; analogous results were obtained with the oxygen electrode. It follows that chromic acid ionizes as a normal dibasic acid. The reaction $H_2CrO_4 \rightleftharpoons H^{\cdot} + HCrO_4{}'$ is almost complete in dil. soln., whereas the reaction $HCrO_4{}' \rightleftharpoons H^{\cdot} + CrO_4{}''$ is extremely small. A. Miolati and E. Mascetti measured the conductivity of soln. of chromic acid during its progressive neutralization with sodium hydroxide; E. Cornec made analogous observations with respect to the f.p., and indices of refraction of soln. of chromic acid being neutralized with sodium, potassium, or ammonium hydroxide; by L. Margaillan, on the e.m.f. of hydrogenized platinum and the soln. against a mercury cathode; and by R. Dubrisay, on the surface tension of the soln. In general, the soln. first forms the dichromate, and as more base is added, the chromate appears. This agrees with the assumption that the aq. soln. contains dichromic acid; and the result was confirmed by the observations of A. K. Datta and N. R. Dhar with respect to the index of refraction, and mol. vol. in soln.; by T. Costa, with respect to the b.p. of the soln.; and by H. C. Jones and H. P. Bassett, with respect to the f.p. of the soln.

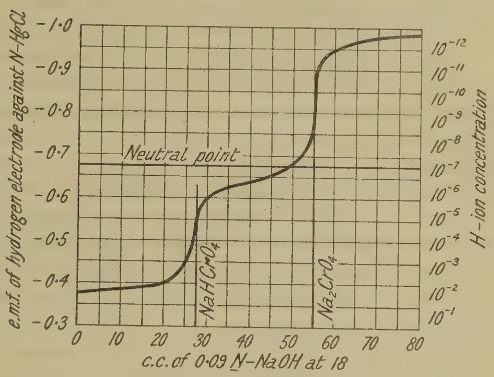


FIG. 26.—Electrometric Titration of Chromic Acid Solutions.

M. S. Sherrill attempted to reconcile the opposing hypothesis as to the nature of the ions in aq. soln. The depression of the f.p. of dil. soln. of chromic acid and potassium dichromate corresponds with their complete ionization into $Cr_2O_7{}''$-, and $H^{\cdot}$- or $K^{\cdot}$-ions, but the presence of some $HCrO_4{}'$-ions was assumed. The **ionization constant** for $2HCrO_4{}' \rightleftharpoons Cr_2O_7{}'' + 2H^{\cdot}$, was $K_1 = [Cr_2O_7{}'']/[HCrO_4{}']^2$, where $K_1 = 27$ with chromic acid soln., and 61 with soln. of potassium dichromate. From observations with ammonium chromate in dil. soln. in the presence of enough ammonia to prevent hydrolysis, $K_2 = [H^{\cdot}][CrO_4{}'']/[HCrO_4{}']$, where $K_2 = 5{\cdot}7 \times 10^{-7}$ at 18°; and from the partition of ammonia between aq. soln. of ammonium chromate, and chloroform, $K_2 = 6{\cdot}2 \times 10^{-7}$ at 18°, and $7{\cdot}4 \times 10^{-7}$ at 25°, so that the strength of chromic acid is about $\frac{1}{30}$th of that of acetic acid. H. T. S. Britton gave $4{\cdot}4 \times 10^{-7}$ for the second ionization constant at 18°; N. R. Dhar gave $K_2 = 5 \times 10^{-8}$; and W. S. Hughes, $K_2 = 10^{-7}$. W. V. Bhagwat and N. R. Dhar studied the subject. For H. Moissan's, and E. H. Riesenfeld and H. E. Wohler's observations on the electrolysis of soln. of chromic acid, *vide infra*, perchromic acid.

Attempts have been made to find the strength of chromic acid relatively with those of other acids. H. Settegast showed spectroscopically that chromic acid is displaced from chromates by sulphuric, formic, acetic, butyric, and tartaric acids. P. Sabatier showed colorimetrically that sulphuric, hydrochloric, phosphoric $H(H_2PO_4)$, and trichloracetic acids completely displace chromic acid from chromates. With acetic acid and the three equal acidic hydrogen atoms of citric acid, the action does not proceed quite so far. It is still less with the first acidic hydrogen of carbonic acid and the second acidic hydrogen of phosphoric acid, whilst the second acidic hydrogen of carbonic acid, boric acid, and the third acidic hydrogen of phosphoric acid have very little action at all. If the normal chromate is treated with an excess of solid boric acid, there is considerable formation of dichromate, owing to the production of an insoluble acid borate, the precipitation of which tends to make the action complete. From thermal data: $(K_2CrO_4,HCl) = 2{\cdot}4$ Cals.; and $(K_2Cr_2O_7,2HCl) = -0{\cdot}2$ Cal., M. Berthelot showed that hydrochloric acid should convert chromates into dichromates. He also found $(K_2CrO_4,6H_2SO_4) = 0{\cdot}76$ Cal.; $(K_2CrO_4,CH_3COOH) = 1{\cdot}5$ Cals.; and $(K_2CrO_4,CO_2) = -0{\cdot}4$ Cal.; and added that in soln. of neutral potassium chromate, strong acids cause the total, and weak acids the partial displacement of one of the two potassium-atoms, potassium dichromate being formed at the same time. This displacement is due not so much to the smaller heat of formation of the chromates compared with other acids capable of displacing chromic acid, as to the fact that the heat of formation of the dichromate is much greater than that of the neutral chromate, and that hence there is always a great tendency to the formation of the dichromate. This tendency renders the one potassium-atom in the neutral chromate easily replaceable—*vide infra,* the action of acids on potassium chromate. W. V. Bhagwat and N. R. Dhar favoured the view that chromic acid exists in soln. as H_2CrO_4, and potassium dichromate as $KHCrO_4$.

E. Spitalsky measured the catalytic effect of soln. of chromic acid on the decomposition of ethyl diazoacetate by G. Bredig's process. Dil. soln. of chromic acid contain almost exclusively the dibasic acid $H_2Cr_2O_7$, which in a dilution of 500 litres is dissociated almost completely into $H^{\cdot}$- and Cr_2O_7''-ions. Dil. soln. of potassium dichromate contain almost exclusively the ions of the normal salt, $K_2Cr_2O_7$. In accordance with this view, dil. soln. of potassium chromate, K_2CrO_4, behave like alkalies to chromic acid, inasmuch as the CrO_4''-ions are changed almost quantitatively into Cr_2O_7''-ions, and the soln. remains neutral. Conc. soln. of potassium dichromate are slightly acid, probably owing to slight hydrolysis according to the equation: $Cr_2O_7''+H_2O\rightleftharpoons 2CrO_4''+2H^{\cdot}$; the corresponding equilibrium constant $K_1=[CrO_4'']^2[H^{\cdot}]^2/[Cr_2O_7'']$ is $5{\cdot}1\times10^{-12}$. In a 0·1 molar soln. of the dichromate, the Cr_2O_7''-ions are hydrolyzed to the extent of 0·13 per cent. and in a 0·017 molar soln. to 0·28 per cent. so that the degree of hydrolysis does not alter much with dilution. Besides the hydrolysis, another reaction represented by the equation $CrO_4''+H^{\cdot}\rightleftharpoons HCrO_4'$ takes place to some extent in dichromate soln.; the corresponding constant $K_2=[CrO_4''][H^{\cdot}]/[HCrO_4']$ is $2{\cdot}7\times10^{-7}$. There is no evidence of the existence in dichromate soln. of complex ions such as Cr_3O_{10}''. J. Sand and K. Kästle showed that the acid resulting from the hydration of chromium trioxide is of medium strength, and suggested that in dichromate soln. there is the hydrolytic equilibrium: $Cr_2O_7''+H_2O\rightleftharpoons 2CrO_4''+2H^{\cdot}$, and in that case, from observations on a mixture of potassium iodate and iodide, the reaction $3Cr_2O_7''+5I'+IO_3'=6CrO_4''+3I_2$ is accelerated by $H^{\cdot}$-ions. The value of $K=[CrO_4'']^2[H^{\cdot}]^2/[Cr_2O_7'']$ calculated from these results is only approximately constant, and amounts to about $K=1{\cdot}5\times10^{-13}$ at 25°; and hence it follows that $0{\cdot}1N$-$K_2Cr_2O_7$ is hydrolyzed to the extent of about 0·18 per cent. The deviation from constancy is not due to the direct action of dichromate on potassium iodide, as the rate of reaction between these substances is much slower than the main reaction. The disturbance is probably due to the catalytic effect of some product formed during the reaction.

J. Lundberg studied the effect of chromate soln. on the hydrolysis of ethyl acetate. If the hydrolysis of potassium chromate proceeds: $CrO_4''+H_2O=HCrO_4'+OH'$, the equilibrium constant $K_1=[HCrO_4'][OH']/[CrO_4'']$; and if $2CrO_4''+H_2O=CrO_7''+2OH'$, then $K_2=[Cr_2O_7'']^{\frac{1}{2}}[OH']/[CrO_4'']$; both values were too irregular to decide which is correct, but conductivity measurements favour the former, and for $0{\cdot}1N$-K_2CrO_4, $K_1=1{\cdot}368\times10^{-7}$, and 0·012 per cent. of the salt is hydrolyzed; and in a $0{\cdot}1N$-$K_2Cr_2O_7$, containing chiefly $HCrO_4'$-ions, the salt is hydrolyzed to the extent of 0·094 per cent. in accord with $HCrO_4'=H^{\cdot}+CrO_4''$. Unlike E. Spitalsky, J. Lundberg assumes that a comparatively large proportion of $HCrO_4'$-ions is present in aq. soln. of potassium dichromate. For the observations of V. K. la Mer and C. L. Read, *vide infra,* sodium dichromate.

Observations on soln. of sparingly soluble chromates and dichromates have been made. Thus, R. Abegg and R. J. Cox studied the hydrolysis of mercuric chromate; M. S. Sherrill, silver chromate; and K. Beck and P. Stegmüller, lead chromate. From these results M. S. Sherrill calculated $[H^{\cdot}][CrO_4'']/[HCrO_4']=8{\cdot}4\times10^{-7}$ at 25° and $[HCrO_4']^2/[Cr_2O_7'']=0{\cdot}013$ at 25°; and K. Beck and P. Stegmüller, $[H^{\cdot}][CrO_4'']/[HCrO_4']=5{\cdot}7\times10^{-7}$ at 18°, and $[HCrO_4']^2/[Cr_2O_7']=2{\cdot}5$ at 18°.

Transport experiments on potassium chromate were made by J. F. Daniell and W. A. Miller, J. W. Hittorf, R. Lenz, O. Masson, B. D. Steele, R. B. Denison, and A. Charpentier; F. Kohlrausch calculated 72 for the **transport number** of $\frac{1}{2}CrO_4''$ from the conductivity data of calcium chromate; and M. S. Sherrill, 76·7 from the data of ammonium chromate; and 40 for the $HCrO_4'$-ion. W. Hittorf, E. H. Riesenfeld, and A. Charpentier made observations with potassium dichromate; and C. W. D. Whetham found the velocity of migration of the Cr_2O_7-ion to be 0·00047 cm. per sec. for a potential difference of one volt; and the transport number to be 91.

F. Morges found that the **electrolysis** of aq. soln. of chromium trioxide furnishes oxygen at the anode, and hydrogen and chromic chromate at the cathode. E. H. Riesenfeld found that in sulphuric acid soln. a perchromic acid is formed at the cathode. According to E. Liebreich, the thin layers of oxide or hydroxide on the cathode, which give rise to the periodic phenomena observed during the electrolysis of chromic acid are colloidal in nature; the oxide is drawn to the cathode just so long as a negative tension lies on it. The addition of chlorides brings about a displacement of two curves which make up the decomposition voltage curve of chromic acid. G. S. Forbes and P. A. Leighton studied the cathodic reduction of chromic acid to a chromic salt, and found the electrochemical yields with the cathode in light were about half per cent. greater than in darkness. Part or all this can be attributed to local heating in the thin diffusion layer above the cathode. The absence of any increase in the photochemical yield in light is compatible with light-sensitive chromate if the latter is equally reactive electrochemically before and after excitation. Granting that the slightly greater electrochemical efficiency in light is in part due to excited chromate, any estimate of the quantum yield requires several assumptions, especially one concerning the life of the excited individual upon which its chance of reaching the cathode depends. The subject was investigated by E. Müller and P. Ekwall, D. T. Ewing and co-workers, and A. Lottermoser and H. Walde. E. Liebreich showed that the thin layers of oxide or hydroxide, formed in the cathode during the electrolysis of soln. of chromic acid, are colloidal; they may give rise to colloidal phenomena; and the addition of chlorides displaces the two curves which make up the decomposition voltage of chromic acid. According to G. P. Vincent, the depolarizing action of a sat. soln. of potassium dichromate on hydrogen liberated at a smooth platinum electrode commences only when about 0·28 per cent. by vol. of conc. sulphuric acid is present. With a clean mercury cathode, the neutral soln. shows 100 per cent. depolarization of the hydrogen set free. The corrosion of zinc, iron, and copper by sat. soln. of potassium dichromate is produced only when the soln. is acidified. No corrosion occurs with sat. soln. of potassium dichromate when copper is short-circuited with mercury or platinum; or when iron is short-circuited with mercury. Zinc when short-circuited with mercury corrodes slightly, and more rapidly in 0·02 per cent. acetic acid soln. than in 0·02 per cent. sulphuric acid soln.

The data of L. Scherbakoff and O. Essin favour the view that in the electrolysis of conc. sulphuric acid soln. of chromic acid chromium is deposited by the discharge of chromic ions, but, according to E. Liebreich, with soln. in dil. acids, the data for current efficiencies favour the view that the metal is deposited by the discharge of chromous ions. S. Takegami studied the anodic oxidation of cathodically reduced chromic acid.

W. D. Bancroft measured the **oxidation potential** of potassium dichromate and chromic acid respectively at 16°–18°, and in $0·2M$-soln. with the following results: stannous chloride and potash-lye, 1·37, and 1·70 volt; stannous chloride and hydrochloric acid, 0·57, and 0·90 volt; sodium sulphide, 1·15, and 1·49 volt; hydroxylamine and potash-lye, 1·12, and — volt; hydroxylamine and hydrochloric acid, 0·43, and — volt; chromous acetate, 0·70, and 1·03 volt; chromous acetate and alkali-lye, 1·09, and — volt; pyrogallol and potash-lye, 0·98, and 1·32 volt; hydroquinone and potash-lye, 0·83, and 1·17 volt; sodium hyposulphite, 0·78, and 1·12 volt; sodium thiosulphate, 0·49, and 0·89 volt; sodium sulphite, 0·48, and 0·81 volt; sodium hydrosulphite, 0·40, and 0·73 volt; sulphurous acid, 0·35, and 0·68 volt; sodium hypophosphite, 0·55, and 0·88 volt; sodium phosphite, 0·47, and 0·80 volt; potassium arsenite, 0·56, and 0·89 volt; potassium ferrous oxalate, 0·78, and — volt. potassium ferrocyanide, 0·47, and 0·80 volt; potassium ferrocyanide and potash-lye, 0·59, and 0·93 volt; iodine and potash-lye, 0·57, and 0·91 volt; ferrous sulphate and sulphuric acid, 0·27, and 0·60 volt; ferrous sulphate, 0·43, and 0·76 volt; and cuprous chloride, 0·50, and 0·84 volt. B. Neumann measured the **potential** of the chromate electrode towards a normal electrode, and found for N-$K_2Cr_2O_7$, 0·79 volt; and for N-$H_2Cr_2O_7$, 1·11 volt. R. Ihle gave for sulphuric acid soln., —1·44 volt, and for alkaline soln., —0·46 volt; W. Hittorf, 1·2 volt; and F. Crotogino, 1·1 to 1·2 volt. The subject was investigated by K. F. Ochs. According to G. S. Forbes and E. P. Bartlett, certain reducing agents increase the oxidation potential of dichromate ions on platinum by amounts up to 0·2 volt—*e.g.* ferrous salts; and, according to L. Loimaranta, iodides. The phenomenon was discussed by R. Abegg, and R. Luther.

R. Luther emphasized the fact brought out by the observations of W. D. Bancroft, and B. Neumann, that the potential of chromic acid, and dichromates is augmented by increasing the acidity of the soln. Thus, if $[H^{\cdot}]$ denotes the conc. of the hydrogen ions, then, the oxidation potentials, E volt, referred to the hydrogen electrode, are:

$[H^{\cdot}]$.	1	0·1	0·01	0·001	0·0001	0·00001	0·000001
E .	1·29	1·05	0·91	0·86	0·81	0·75	0·66

The chromic oxide-chromic acid potential given by R. Abegg and co-workers for $Cr^{\cdot\cdot\cdot}+4H_2O+3\oplus\rightleftharpoons HCrO_4'+7H^{\cdot}$ is nearly 1·3 volt. In alkaline soln., the potential referred to the normal electrode for $Cr(OH)_{3solid}+5OH'+3\oplus\rightleftharpoons CrO_4''+4H_2O$, is —0·1 volt, and E. Müller gave 0·908 for the e.m.f. of the cell Pt | H_2, 0·01N-KOH | 0·01N-KOH, 0·025K_2CrO_4 | Pt. E. Spitalsky found the potential of a dichromate soln. to be about 0·85 volt in the presence of an $H^{\cdot}$-ion concentration of 10^{-3} to 10^{-4}. R. Luther observed that the oxidation of chromium, and bi- and ter-valent chromium to chromate ions yield an e.m.f. corresponding with 0·6 volt for $Cr_{metal}\rightarrow CrO_4''$ against a normal electrode; 1·1 volt for $Cr^{\cdot\cdot}\rightarrow CrO_4''$; and 1·5 volt for $Cr^{\cdot\cdot\cdot}\rightarrow CrO_4''$. In acidic soln., the CrO_4''-ion plays only a secondary part. In the case of $HCrO_4'$-ions, the e.m.f. are 0·4 volt for $Cr_{metal}+4H_2O+6\oplus\rightarrow HCrO_4'+7H^{\cdot}$; 0·9 volt for $Cr^{\cdot\cdot}+4H_2O+4\oplus\rightarrow HCrO_4'+7H^{\cdot}$; and 1·3 volt for $Cr^{\cdot\cdot\cdot}+4H_2O+3\oplus\rightarrow HCrO_4'+7H^{\cdot}$. These changes furnish $Cr_{metal}\rightarrow Cr^{\cdot\cdot}$, 0·3 volt; $Cr_{metal}\rightarrow Cr^{\cdot\cdot\cdot}$, 0·2 volt; $Cr^{\cdot\cdot}\rightarrow Cr^{\cdot\cdot\cdot}$, 0·1 volt. If an intermediate oxidation compound exists under the conditions of observation, this compound is a stronger oxidizing agent than the highest oxidation product, and a stronger reducing agent than the lowest oxidation product.

H. Moissan[8] said that aq. soln. of chromium trioxide are **photosensitive,** for they decompose with the evolution of oxygen, when exposed to light. M. Ponton found that although chromates are stable in light, they are rapidly reduced if organic substances be present—*e.g.* ammonium or potassium dichromate in contact with paper. J. M. Eder observed that glue, albumin, gum arabic, dextrine, cane-sugar, grape-sugar, glycerol, caseïn, alcohol, etc., act in this way. E. Kopp said that chromic oxide is formed. The reaction was observed by W. H. F. Talbot, A. Poitevin, and J. C. Schnauss. E. Goldberg said that the reaction between quinine and chromates is activated by light; but R. Luther and G. S. Forbes showed that the photoactivation of the chromate is negligibly small in comparison with that of the quinine. The subject was discussed by J. Plotnikoff, H. C. Winther, E. J. Bowen and C. W. Bunn, H. Zocher and K. Coper, B. K. Mukerji and N. R. Dhar, F. Weigert, G. S. Forbes and co-workers, M. Schiel, F. Schömmer, G. S. Forbes and P. A. Leighton, and R. E. Liesegang. J. Plotnikoff found that the chromate of ammonium, potassium or sodium suffers no decomposition when exposed to the most intense sunlight provided substances capable of oxidation are absent; if organic substances are present, reduction occurs even in the light from an electric arc; the reduction results in the formation of a brown precipitate or of a green soln. according to the nature of the oxygen acceptor; and gas may be evolved in some cases—*e.g.* ammonia from ammonium chromate. The photosensitiveness of mixtures of gelatine or glue and chromates is of industrial importance—the organic substance becomes insoluble and the chromium trioxide is reduced. J. M. Eder showed that in this respect, the dichromates are more sensitive than the chromates. A. Popovicky suggested that the substance obtained when gelatin treated with a dichromate is exposed to sunlight is the compound, $4Cr_2O_3.3CrO_3$; the tanning action on gelatin is attributed to this compound. J. M. Eder found that the action of light on chromated gelatin begins at $550\mu\mu$, reaches a maximum between $470\mu\mu$ and $430\mu\mu$, and becomes very slight beyond $380\mu\mu$. This is in contrast with J. Plotnikoff's result with collodion sensitized with potassium dichromate and cresyl-blue in which the action was found to begin in the yellow at $595\mu\mu$, and reached a maximum in the green between $540\mu\mu$ and $580\mu\mu$. A photographic reproduction process is based on the reaction; and chromated and insolated glue can in some cases be used as a substitute for wood, leather, or celluloid. According to T. Swensson, the potential of soln. of potassium dichromate against a platinum electrode, and exposed to the ultra-violet light of a mercury lamp, rises rapidly, and on removing the light, it slowly falls. The same result is obtained whether or not the platinum electrode is illuminated. A soln. with 4 mols of sulphuric acid and a mol of potassium dichromate per litre, gives an increase of potential of 0·2280 volt by illumination. The cause of the large change in potential is in some way due to a mutual action of the dichromate and sulphuric acid, since both potassium dichromate soln. and sulphuric acid when submitted alone to the action of the light only give a lowering of the potential, whereas chromic acid soln. gives a slight increase. The increase of potential is independent of the conc. of the soln. E. Müller studied the potential-current curves of 30 per cent. soln. of chromium trioxide, from which it is inferred that a film of chromic oxide is formed at cathode potentials not exceeding 0·3 volt. This film hinders the excess of chromium ions, but is permeable to hydrogen ions. At about —0·7 volt, the film begins to be permeable and an almost continuous reduction of sexivalent to tervalent chromium sets in; and with still more negative values, the deposition of chromium begins, and the film disappears. In the presence of SO_4-, NO_3-, ClO_4-, and SiF_6-ions, the film is imperfect and may be swept away by the gaseous hydrogen which is evolved—hence the presence of sulphates favours the deposition of bright, coherent chromium. The periodic phenomenon in the electrolysis of chromic acid was discussed by J. E. Liebreich, G. J. Sargent, A. Kleffner, and K. Oyabu. A. V. Pamfiloff discussed the *rôle* of chromates in the electroytic production of chlorates; and D. J. MacNaughtan and R. A. F. Hammond, in the electrodeposition of nickel.

According to E. Wedekind and C. Horst,[9] the **magnetic susceptibility** of chromium trioxide is $0{\cdot}75\times10^{-6}$ mass units; K. Honda and T. Sone gave $0{\cdot}51\times10^{-6}$ at 18°, and at 225°, L. Blanc, and L. A. Welo made some observations on this subject. P. Pascal gave $-0{\cdot}5\times10^{-5}$ for the mol. magnetic susceptibility of chromic acid.

REFERENCES.

[1] O. Unverdorben, *Trommsdorff's Journ.*, **9**. 26, 1824; *Pogg. Ann.*, **7**. 311, 1926; K. F. W. Meissner, *Gilbert's Ann.*, **60**. 366, 1818; J. J. Berzelius, *Schweigger's Journ.*, **22**. 53, 1818; *Pogg. Ann.*, **1**. 34, 1824; *Ann. Chim. Phys.*, (2), **17**. 7, 1821; F. Kuhlmann, *ib.*, (3), **54**. 400, 1858; L. N. Vauquelin, *ib.*, (1), **70**. 70, 1809, A. Mussin-Puschkin, *Crell's Ann.*, i, 355, 1798; H. Moser, *Chemische Abhandlung über das Chrom*, Wien, 1824; *Schweigger's Journ.*, **42**. 99, 1824; J. B. Richter, *Ueber die neueren Gegenstände der Chymie*, Breslau, **10**. 30, 1802; *Gehlen's Journ.*, **5**. 351, 1805; J. Thomsen, *Pogg. Ann.*, **140**. 513, 1870; E. Zettnow, *ib.*, **143**. 468, 1871; A. Maus, *ib.*, **9**. 127, 1827; J. Krutwig, *Ber.*, **14**. 306, 1881; F. Mylius and R. Funk, *ib.*, **33**. 3686, 1900; J. Fritzsche, *Pogg. Ann.*, **50**. 549, 1840; *Journ. prakt. Chem.*, (1), **19**. 176, 1840; *Mém. Acad. St. Petersburg*, **6**. 181, 1839; R. Warington, *Phil. Mag.*, (3), **20**. 453, 1842;

O. Ficinus, *Arch. Pharm.*, (2), **3**. 23, 305, 1873 ; G. Vulpius, *ib.*, (3), **24**. 954, 1886 ; A. Dietze, *Pharm. Ztg.*, **42**. 346, 1897 ; A. Schafarik, *Sitzber. Akad. Wien*, **47**. 254, 1863 ; *Journ. prakt. Chem.*, (1), **90**. 12, 1863 ; M. Traube, *Liebig's Ann.*, **66**. 87, 165, 1848 ; P. A. Bolley, *ib.*, **56**. 113, 1845 ; R. Bunsen, *ib.*, **148**. 290, 1868 ; E. Hintz, *ib.*, **169**. 368, 1873 ; A. Schrötter, *ib.*, **48**. 225, 1843 ; *Pogg. Ann.*, **59**. 616, 1843 ; R. Böttger, *Journ. prakt. Chem.*, (1), **30**. 263, 1843 ; H. Moissan, *Ann. Chim. Phys.*, (6), **5**. 568, 1885 ; *Compt. Rend.*, **98**. 1581, 1884 ; E. Duvillier, *ib.*, **75**. 711, 1872 ; **76**. 1353, 1873 ; A. Mailfert, *ib.*, **94**. 863, 1882 ; M. Siewert, *Zeit. ges. Naturwiss.*, **19**. 11, 1862 ; W. A. Rowell, *Brit. Pat. No.* 1283, 1884 ; D. G. Fitzgerald and B. C. Molloy, *Brit. Pat. No.* 266, 1874 ; T. Costa, *Gazz. Chim. Ital.*, **36**. i, 535, 1906 ; E. Field, *Chem. News*, **65**. 153, 1892 ; *Journ. Chem. Soc.*, **61**. 405, 1892 ; F. Fichter and E. Brunner, *ib.*, 1862, 1928 ; J. Voisin, *Rev. Mét.*, **7**. 1143, 1910 ; G. Wyrouboff, *Bull. Soc. Chim.*, (4), **5**. 765, 1909 ; A. J. Balard, *Ann. Chim. Phys.*, (2), **57**. 225, 1834 ; *Taylor's Scientific Memoirs*, **1**. 269, 1837 ; E. Müller and M. Soller, *Zeit. Elektrochem.*, **11**. 863, 1905 ; P. Askenasy and A. Révai, *ib.*, **19**. 344, 1913 ; M. Prud'homme and F. Binder, *Bull. Soc. Chim.*, (2), **37**. 194, 1882 ; G. P. Baxter, E. Mueller and M. A. Hines, *Journ. Amer. Chem. Soc.*, **31**. 529, 1909 ; J. Milbauer, *Chem. Ztg.*, **40**. 587, 1916 ; G. Chancel, *Compt. Rend.*, **43**. 927, 1856 ; S. Cloez and E. Guignet, *ib.*, **47**. 710, 1858 ; H. Vohl, *Liebig's Ann.*, **68**. 398, 1847 ; F. H. Storer, *Proc. Amer. Acad.*, **4**. 338, 1859 ; *Chem. News*, **1**. 253, 265, 301, 1860 ; F. Melde, *Pogg. Ann.*, **124**. 91, 1865 ; E. Lenssen, *Journ. prakt. Chem.*, (1), **81**. 280, 1860 ; M. Holzmann, *ib.*, (1), **75**. 340, 1858 ; A. Reynoso, *Ann. Chim. Phys.*, (3), **33**. 324, 1851 ; A. V. Rakowsky, *Journ. Russ. Phys. Chem. Soc.*, **60**. 13, 1928 ; J. W. Döbereiner, *Schweigger's Journ.*, **22**. 476, 1818 ; O. W. Gibbs, *Amer. Journ. Science*, (3), **5**. 110, 1873 ; D. Meneghini, *Gazz. Chim. Ital.*, **42**. i, 134, 1912 ; A. Terni, *ib.*, **43**. ii, 63, 1913 ; E. Bohlig, *Zeit. anal. Chem.*, **9**. 357, 1870 ; M. Salinger, *Zeit. anorg. Chem.*, **33**. 342, 1903 ; H. Marshall, *Journ. Soc. Chem. Ind.*, **16**. 396, 1897 ; D. M. Yost, *Journ. Amer. Chem. Soc.*, **48**. 152, 1926 ; A. R. y Miro, *Anal. Fis. Quim.*, **20**. 684, 1922 ; A. Dalzell, *B.A. Rep.*, 68, 1859 ; K. Fischbeck and E. Einecke, *Zeit. anorg. Chem.*, **167**. 21, 1927 ; O. Stumm, *Ueber Oxydation des Chrom—(III)—hydroxyds in wässrig-alkalinischer Lösung durch molekularen Sauerstoff*, Leipzig, 1928 ; Metals Protection Corporation, *Brit. Pat. No.* 307061, 1929 ; V. V. Polyanksy, *Trans. Inst. Pure Chem. Reagents*, 300, 1929 ; J. J. Lichtin, *Journ. Ind. Eng. Chem.—Anal.*, **2**. 126, 1930.

[2] J. Koppel and R. Blumenthal, *Zeit. anorg. Chem.*, **53**. 262, 1906 ; R. Luther and T. F. Rutter, *ib.*, **54**. 1, 1907 ; E. Spitalsky, *ib.*, **54**. 265, 1907 ; K. Seubert and J. Carstens, *ib.*, **58**. 357, 1908 ; F. Mylius and R. Funk, *Ber.*, **33**. 3686, 1900 ; *Wiss. Abh. Phys. Tech. Reichsanst.*, **3**. 451, 1900 ; R. Kremann, *Sitzber. Akad. Wien*, **120**. 339, 1911 ; H. Moissan, *Compt. Rend.*, **98**. 1582, 1884 ; *Ann. Chim. Phys.*, (6), **5**. 568, 1885 ; J. J. Berzelius, *Jahresber.*, **6**. 130, 1827 ; *Schweigger's Journ.*, **22**. 53, 1818 ; *Pogg. Ann.*, **1**. 34, 1824 ; *Ann. Chim. Phys.*, (2), **17**. 7, 1821 ; T. Costa, *Gazz. Chim. Ital.*, **36**. i, 535, 1892 ; E. Field, *Journ. Chem. Soc.*, **61**. 405, 1892 ; *Chem. News*, **65**. 153, 1892 ; W. Ostwald, *Zeit. phys. Chem.*, **2**. 79, 1888 ; R. Abegg and A. J. Cox, *ib.*, **48**. 725, 1904 ; E. H. Büchner and A. Prins, *ib.*, **81**. 113, 1913 ; H. Settegast, *Wied. Ann.*, **7**. 242, 1879 ; M. S. Sherrill, *Journ. Amer. Chem. Soc.*, **29**. 1641, 1907 ; L. N. Vauquelin, *Journ. Phys.*, **45**. 393, 1794 ; **46**. 152, 311, 1798 ; *Journ. Mines*, **6**. 737, 1797 ; *Nicholson's Journ.*, **2**. 387, 441, 1799 ; *Phil. Mag.*, **1**. 279, 361, 1798 ; **2**. 74, 1798 ; *Ann. Chim. Phys.*, (1), **25**. 21, 194, 1798 ; (1), **70**. 70, 1809 ; S. M. Godon de St. Menin, *ib.*, (1), **63**. 222, 1805 ; *Ann. Musée Hist. Nat.*, **4**. 238, 1804 ; *Phil. Mag.*, **20**. 266, 1805 ; H. Lessheim, J. Meyer and R. Samuel, *Zeit. Physik*, **43**. 299, 1927 ; C. F. Rammelsberg, *Pogg. Ann.*, **127**. 492, 1866 ; A. Schrötter, *ib.*, **59**. 616, 1843 ; *Liebig's Ann.*, **48**. 225, 1843 ; W. Manchot, *Ber.*, **39**. 1354, 1906 ; A. Geuther, *Lehrbuch der Chemie*, Jena, 385, 1870 ; A. Werner, *Neuere Anschauungen auf dem Gebiete der anorganische Chemie*, Braunschweig, 63, 1905 ; H. C. Jones, *Hydrates in Aqueous Solution*, Washington, 98, 1907 ; G. F. Hüttig and B. Kurre, *Zeit. anorg. Chem.*, **126**. 167, 1923 ; R. Weinland and H. Staelin, *ib.*, **136**. 313, 1924 ; A. Miolatti, *Journ. prakt. Chem.*, (2), **77**. 444, 1908 ; F. Auerbach, *Zeit. anorg. Chem.*, **126**. 54, 1923 ; W. V. Bhagwat and N. R. Dhar, *Journ. Indian Chem. Soc.*, **6**. 781, 1929 ; N. R. Dhar, *Zeit. anorg. Chem.*, **121**. 99, 1922 ; P. Niggli, *Zeit. Kryst.*, **75**. 278, 1930.

[3] A. E. Nordenskjöld, *Oefvers. Förh. Stockholm*, **17**. 439, 1860 ; *Pogg. Ann.*, **114**. 612, 1861 ; E. Zettnow, *ib.*, **143**. 474, 1871 ; J. R. Partington and S. K. Tweedy, *Journ. Chem. Soc.*, 2900, 1927 ; L. Playfair and J. P. Joule, *Mem. Chem. Soc.*, **3**. 82, 1848 ; A. Schafarik, *Sitzber. Akad. Wien*, **47**. 254, 1863 ; *Journ. prakt. Chem.*, (1), **90**. 12, 1863 ; D. Balareff, *ib.*, (2), **102**. 283, 1921 ; G. G. and I. N. Longinescu, *Bull. Soc. Romana, Stiinte*, **26**. 1, 1923 ; C. H. D. Bödeker, *Die Beziehungen zwischen Dichte und Zusammensetzung bei festen und liquiden Stoffen*, Leipzig, 1860 ; H. C. Jones and H. P. Bassett, *Amer. Chem. Journ.*, **34**. 334, 1905 ; H. C. Jones, *Hydrates in Aqueous Solution*, Washington, 99, 1907 ; C. del Fresno, *Anal. Fis. Quim.*, **24**. 707, 1926 ; D. I. Mendeléeff, *Études des dissolutions aqueuses*, St. Petersburg, 1887 ; F. Rinne, *Neues Jahrb. Min.*, i, 171, 1900 ; R. Dubrisay, *Compt. Rend.*, **156**. 894, 1902, 1913 ; S. A. Mumford and L. F. Gilbert, *Journ. Chem. Soc.*, **123**. 471, 1923 ; T. Graham, *Phil. Trans.*, **140**. 1, 805, 1850 ; **141**. 483, 1851 ; *Journ. Chem. Soc.*, **3**. 60, 1851 ; *Phil. Mag.*, (3), **37**. 181, 254, 341, 1850 ; J. J. Coleman, *ib.*, (5), **23**. 1, 1887 ; H. R. Moore and W. Blum, *Journ. Research Bur. Standards*, **5**. 255, 1930 ; W. Biltz, *Zeit. anorg. Chem.*, **193**. 321, 1930 ; W. A. Roth and G. Becker, *Zeit. phys. Chem.*, **145**. 461, 1930 ; C. del Fresno, *Zeit. Elektrochem.*, **36**. 163, 1930 ; *Ann. Fis. Quim.*, **24**. 707, 1926.

[4] J. C. G. de Marignac, *Ann. Chim. Phys.*, (5), **8**. 418, 1876 ; W. G. Mixter, *Amer. Journ. Science*, (4), **26**. 125, 1908 ; H. C. Jones, *Hydrates in Aqueous Solution*, Washington, 99, 1907 ;

H. C. Jones and H. P. Bassett, *Amer. Chem. Journ.*, **34**. 334, 1905 ; J. Koppel and R. Blumenthal, *Zeit. anorg. Chem.*, **53**. 248, 1907 ; H. Arctowsky, *ib.*, **9**. 29, 1895 ; E. Groschuff, *ib.*, **58**. 102, 1908 ; E. H. Büchner and A. Prins, *Zeit. phys. Chem.*, **81**. 114, 1912 ; L. and P. Wöhler, *ib.*, **62**. 440, 1908 ; A. Berkenheim, *ib.*, **135**. 231, 1928 ; I. Schukoff, *Journ. Russ. Phys. Chem. Soc.*, **4**. 302, 1909 ; *Compt. Rend.*, **148**, 1396, 1908 ; R. Read, *Chem. News*, **95**. 169, 1907 ; A. Simon and T. Schmidt, *Zeit. anorg. Chem.*, **153**. 191, 1924 ; N. de Kolossowsky, *Journ. Chim. Phys.*, **22**. 225, 1925 ; F. Morges, *Compt. Rend.*, **86**. 1443, 1878 ; P. Sabatier, *ib.*, **103**. 267, 1886 ; M. Berthelot, *ib.*, **96**. 541, 1883 ; *Ann. Chim. Phys.*, (6). **1**. 108, 1884 ; H. Moissan, *ib.*, (6), **5**. 568, 1885 ; *Compt. Rend.*, **98**. 1581, 1884 ; J. Thomsen, *Thermochemische Untersuchungen*, **1**. 255, 1882 ; **2**. 464, 1882 ; E. Cornec, *Contribution à l'étude physicochimique de la neutralisation*, Paris, 1912 ; *Ann. Chim. Phys.*, (5), **28**. 697, 1913 ; (8), **29**. 490, 1913 ; (8), **30**. 63, 1913 ; *Compt. Rend.*, **149**. 676, 1909 ; J. J. Berzelius, *Schweigger's Journ.*, **22**. 53, 1818 ; *Pogg. Ann.*, **1**. 34, 1824 ; *Ann. Chim. Phys.*, (2), **17**. 7, 1821 ; E. Field, *Journ. Chem. Soc.*, **61**. 405, 1892 ; *Chem. News*, **65**. 153, 1892 ; A. Schafarik, *Sitzber. Akad. Wien*, **47**. 254, 1863 ; *Journ. prakt. Chem.*, (1), **90**. 12, 1863 ; T. Costa, *Gazz. Chim. Ital.*, **36**. i, 535, 1892 ; O. Unverdorben, *Trommsdorff's Journ.*, **9**. 26, 1824 ; *Pogg. Ann.*, **7**. 311, 1826 ; W. Ostwald, *Zeit. phys. Chem.*, **2**. 79, 1888 ; E. Zettnow, *Pogg. Ann.*, **143**. 468, 1871 ; R. Abegg and A. J. Cox, *Zeit. phys. Chem.*, **48**. 725, 1904 ; E. Hintz, *Liebig's Ann.*, **169**. 368, 1873 ; K. S. Nargund and H. E. Watson, *Journ. Indian Inst. Science*, **7**. 149, 1926 ; F. M. Jäger and H. C. Germs, *Zeit. anorg. Chem.*, **119**. 145, 1921 ; H. C. Germs, *De thermische Analyse van Loodsulfaat, -Chromaat, -Molybdaat en -Wolframaat en van hun binaire Combinaties*, Groningen, 1917 ; M. Traube, *Liebig's Ann.*, **66**. 165, 1847 ; W. A. Roth and G. Becker, *Zeit. phys. Chem.*, **145**. 461, 1930.

[5] W. J. Pope, *Journ. Chem. Soc.*, **69**. 1530, 1896 ; J. Piccard and E. Thomas, *Helvetica Chim. Acta*, **6**. 1040, 1923.

[6] J. H. Gladstone, *Phil. Mag.*, (4), **14**. 418, 1857 ; *Journ. Chem. Soc.*, **10**. 79, 1858 ; D. Brewster, *Phil. Mag.*, (4), **24**. 441, 1862 ; A. Étard, *Compt. Rend.*, **120**. 1057, 1895 ; G. Massol and A. Faucon, *ib.*, **157**. 332, 1913 ; P. Sabatier, *ib.*, **103**. 49, 1886 ; *Journ. Phys.*, (2), **6**. 312, 1887 ; J. M. Hiebendaal, *Oriderzoek over eenige absorptic spectra*, Utrecht, 1873 ; F. Weigert, *Ber.*, **49**. 1519, 1916 ; H. Settegast, *Wied. Ann.*, **7**. 242, 1879 ; O. Knoblauch, *ib.*, **43**. 738, 1891 ; P. Glan, *ib.*, **3**. 54, 1878 ; W. Böhlendorff, *Studien zur Absorptionsspectralanalyse*, Erlangen, 1890 ; B. K. Mukerji, A. K. Bhattacharji, and N. R. Dhar, *Journ. Phys. Chem.*, **32**. 1834, 1928 ; A. M. Taylor, *Trans. Faraday Soc.*, **25**. 856, 1929 ; K. Vierordt, *Die Anwendung des Spectralapparates zur Photometrie*, Tübingen, 1873 ; F. Grünbaum, *Zur Photometrie der Absorptionsspektren von Lösungen*, Berlin, 1902 ; *Ann. Physik*, (4), **12**. 1009, 1903 ; H. Becquerel, *Ann. Chim. Phys.*, (5), **30**. 5, 1883 ; H. M. Vernon, *Chem. News*, **66**. 104, 114, 141, 152, 1892 ; J. L. Soret, *Arch. Sciences Genève*, (2), **61**. 322, 1878 ; J. Formánek, *Die qualitative Spectralanalyse anorganischer Körper*, Berlin, 1900 ; H. Bremer, *Einfluss der Temperatur gefärbter Lösungen auf die Absorptionsspectra derselben*, Erlangen, 1890 ; F. Melde, *Pogg. Ann.*, **124**. 91, 1865 ; J. Müller, *ib.*, **72**. 76, 1847 ; C. P. Smyth, *Trans. Edin. Roy. Soc.*, **28**. 779, 1879 ; A. Hantzsch, *Zeit. phys. Chem.*, **72**. 362, 1910 ; A. Hantzsch and R. H. Clark, *ib.*, **63**. 367, 1908 ; A. Hantzsch and C. S. Garrett, *ib.*, **84**. 321, 1913 ; H. von Halban and H. Siedentopf, *ib.*, **100**. 208, 1922 ; G. Jander and T. Aden, *ib.*, **144**. 197, 1929 ; H. C. Jones and W. W. Strong, *The Absorption Spectra of Solutions*, Washington, 1911 ; *A Study of Absorption Spectra of Solutions*, Washington, 1910 ; *Amer. Chem. Journ.*, **43**. 37, 1910 ; *Phys. Zeit.*, **10**. 499, 1909 ; W. Spring, *Rec. Trav. Chim. Pays-Bas*, **29**. 163, 1910 ; *Bull. Soc. Chim. Belg.*, **24**. 109, 1910 ; *Bull. Acad. Belg.*, 11, 1910 ; *Arch. Sciences Genève*, (4), **29**. 145, 1910 ; G. Rudorf, *Lichtabsorption in Lösungen vom Standpunkte der Dissoziationstheorie*, Stuttgart, 1904 ; P. Pogány, *Tables annuelles de constantes et données numériques*, Paris, **2**. 132, 1911 ; *Szinezö iónok és molekulák egyeneulyának vezsgálata spectrophotometrias úton*, Budapest, 1908 ; E. Cornec, *Contribution à l'étude physicochimique de la neutralization*, Paris, 1912 ; *Ann. Chim. Phys.*, (5), **28**. 697, 1913 ; (8), **29**. 490, 1913 ; (8), **30**. 63, 1913 ; *Compt. Rend.*, **149**. 676, 1909 ; A. Karl, *ib.*, **146**. 1104, 1908 ; R. Robl, *Zeit. angew. Chem.*, **39**. 608, 1916 ; E. Viterbi and G. Krausz, *Gazz. Chim. Ital.*, **57**. 690, 1927 ; W. S. Hughes, *Journ. Chem. Soc.*, 491, 1928 ; N. R. Tawde and G. R. Paranjpe, *Indian Journ. Phys.*, **4**. 533, 1930 ; H. Nisi, *Japan. Journ. Phys.*, **5**. 119, 1929 ; D. M. Yost, *Phil. Mag.*, (7), **8**. 845, 1929 ; G. Jander and T. Aden, *Zeit. phys. Chem.*, **143**. 197, 1929 ; M. N. Saha, *Nature*, **125**. 163, 1930 ; C. P. Snow and F. I. G. Rawlins, *ib.*, **125**. 349, 1930 ; P. Bovis, *Rev. Opt.*, **7**. 434, 1928.

[7] H. Buff, *Liebig's Ann.*, **110**. 257, 1859 ; L. Bleekrode, *Wied. Ann.*, **3**. 170, 1878 ; *Phil. Mag.*, (5), **5**. 375, 439, 1878 ; J. W. Hittorf, *Wied. Ann.*, **4**. 403, 1878 ; R. Lenz, *Mém. Acad. St. Petersburg*, (7), **26**. 3, 1879 ; (7), **30**. 64, 1882 ; P. Walden, *Zeit. phys. Chem.*, **1**. 547, 1887 ; **2**. 71, 1888 ; R. Abegg and A. J Cox, *ib.*, **48**. 725, 1904 ; W. Ostwald, *ib.*, **2**. 79, 1888 ; W. D. Bancroft, *ib.*, **10**. 387, 1892 ; B. Neumann, *ib.*, **14**. 193, 1894 ; R. Luther, *ib.*, **30**. 652, 1899 ; *Zeit. Elektrochem.*, **13**. 289, 1907 ; E. Müller and P. Ekwall, *ib.*, **35**. 84, 1929 ; R. Luther and T. F. Rutter, *Zeit. anorg. Chem.*, **54**. 1, 1907 ; H. C. Jones and H. P. Bassett, *Amer. Chem. Journ.*, **34**. 334, 1905 ; H. C. Jones and C. A. Jacobson, *ib.*, **40**. 355, 1908 ; H. C. Jones, *Hydrates in Solution*, Washington, 98, 1907 ; H. T. S. Britton, *Journ. Chem. Soc.*, **125**. 1572, 1924 ; E. Spitalsky, *Zeit. anorg. Chem.*, **54**. 265, 1907 ; A. Lottermoser and H. Walde, *ib.*, **134**. 368, 1924 ; J. Lundberg, *ib.*, **55**. 426, 1907 ; F. Crotogino, *ib.*, **24**. 225, 1900 ; E. Müller, *ib.*, **26**. 76, 1901 ; J. Sand and K. Kästle, *ib.*, **52**. 101, 1907 ; J. Sand, *Ber.*, **39**. 2038, 1906 ; W. Spring, *Rev. Trav. Chim. Pays-Bas*, **29**. 163, 1910 ; *Bull. Acad. Belg.*, 11, 1910 ; *Bull. Soc. Chim. Belg.*, **24**. 109, 1910 ; *Arch. Sciences Genève*, (4), **29**. 145, 1910 ; E. Bouty, *Compt. Rend.*,

98. 140, 1884 ; F. Morges, *ib.*, **87**. 15, 1878 ; L. Margaillan, *ib.*, **157**. 994, 1913 ; R. Dubrisay, *ib.*, **156**. 1902, 1913 ; E. Carrière and P. Castel, *ib.*, **187**. 1292, 1928 ; A. Charpentier, *ib.*, **136**. 1652, 1903 ; P. Sabatier, *ib.*, **103**. 138, 1886 ; *Bull. Soc. Chim.*, (2), **46**. 294, 1886 ; M. Berthelot, *Ann. Chim. Phys.*, (6), **6**. 506, 1885 ; *Compt. Rend.*, **96**. 401, 1883 ; **100**. 207, 1885 ; G. Bredig, *Biochem. Zeit.*, **6**. 290, 1907 ; W. C. D. Whetham, *Proc. Roy. Soc.*, **66**. 192, 1900 ; **71**. 332, 1903 ; *Zeit. phys. Chem.*, **11**. 220, 1893 ; **33**. 344, 1903 ; R. Ihle, *ib.*, **22**. 120, 1897 ; T. Svensson, *ib.*, **91**. 624, 1916 ; *Arkiv Kem. Min. Geol.*, **6**. 12, 1917 ; E. H. Riesenfeld and H. E. Wohlers, *Ber. naturforsch. Ges. Freiburg*, **17**. 1, 1907 ; E. H. Riesenfeld, *Zeit. Elektrochem.*, **7**. 645, 1901 ; E. Müller, *ib.*, **32**. 399, 1926 ; A. Kleffner, *ib.*, **29**. 488, 1923 ; K. Oyabu, *ib.*, **29**. 49, 1923 ; R. Abegg, *ib.*, **13**. 289, 1907 ; R. Abegg, F. Auerbach and R. Luther, *Messungen elektromotorischer Kräfte galvanischer Ketten*, Halle, 1911 ; A. V. Pamfiloff, *Bull. Inst. Polyt. Ivanovo-Voznesensk*, **4**. 113, 1921 ; E. Liebreich, *Zeit. Elektrochem.*, **27**. 94, 452, 1921 ; **29**. 208, 1923 ; **30**. 186, 1924 ; G. J. Sargent, *Trans. Amer. Electrochem. Soc.*, **37**. 479, 1920 ; G. P. Vincent, *Journ. Phys. Chem.*, **29**. 875, 1925 ; N. H. Furman, *Journ. Amer. Chem. Soc.*, **44**. 2685, 1922 ; F. Kohlrausch, *Zeit, Elektrochem.*, **13**. 333, 1907 ; **14**. 129, 1908 ; *Wied. Ann.*, **50**. 385, 1893 ; **86**. 785, 1898 ; *Sitzber. Akad. Berlin*, 1002, 1900 ; 1026, 1901 ; 572, 1902 ; R. N. J. Saal, *Rec. Trav. Chim. Pays-Bas*, **47**. 264, 1928 ; E. H. Riesenfeld, *Zur Kenntnis der Ueberchromsäuren und ihrer Salze*, Freiburg, 1906 ; L. Loimaranta, *Zeit. Elektrochem.*, **13**. 33, 1907 ; I. Scherbakoff and O. Essin, *ib.*, **33**. 245, 1927 ; E. Liebreich, *ib.*, **34**. 41, 1928 ; W. V. Bhagwat and N. R. Dhar, *Journ. Indian Chem. Soc.*, **6**. 781, 1929 ; T. Costa, *Gazz. Chim. Ital.*, **36**. i, 535, 1892 ; A. Miolati and E. Mascetti, *ib.*, **31**. 93, 116, 1901 ; M. S. Sherrill, *Journ. Amer. Chem. Soc.*, **29**. 1641, 1907 ; N. R. Dhar, *Zeit. anorg. Chem.*, **121**. 99, 1921 ; A. K. Datta and N. R. Dhar, *Journ. Amer. Chem. Soc.*, **38**. 1303, 1917 ; G. S. Forbes and E. P. Bartlett, *ib.*, **35**. 1527, 1913 ; W. S. Hughes, *ib.*, **44**. 2860, 1922 ; D. T. Ewing, J. D. Hardesty and Te Hsia Kao, *Bull. Eng. Exp. Station, Michigan Coll.*, 19, 1928 ; Y. Kato and T Murakami, *Chem. News*, **137**. 323, 1928 ; N. R. Dhar, *Journ. Indian Chem. Soc.*, **5**. 585, 1928 ; G. S. Forbes and P. A. Leighton, *Journ. Phys. Chem.*, **30**. 1628, 1926 ; K. Beck and P. Stegmüller, *Arb. Gesund. Amt.*, **34**. 446, 1910 ; E. Cornec, *Contribution à l'étude physico-chimique de la neutralisation*, Paris, 1912 ; *Ann. Chim. Phys.*, (5), **28**. 697, 1913 ; (8), **29**. 490, 1913 ; (8), **30**. 63, 1913 ; *Compt. Rend.*, **149**. 676, 1909 ; J. F. Daniell and W. A. Miller, *Phil. Trans.*, **124**. 1, 1844 ; O. Masson, *ib.*, **192**. 331, 1899 ; *Zeit. phys. Chem.*, **29**. 501, 1898 ; R. B. Denison, *ib.*, **44**. 575, 1903 ; W. Hittorf, *Pogg. Ann.*, **106**. 337, 513, 1859 ; *Zeit. phys. Chem.*, **30**. 481, 1899 ; B. D. Steele, *Journ. Chem. Soc.*, **79**. 414, 1901; *Zeit. Elektrochem.*, **7**. 618, 1901 ; *Zeit. phys. Chem.*, **40**. 689, 1902 ; *Phil. Trans.*, **198**, 105, 1902 ; H. Settegast, *Wied. Ann.*, **7**. 242, 1879 ; H. Moissan, *Compt. Rend.*, **97**. 96, 1883 ; K. F. Ochs, *Ueber Oxydations- und Reduktionsketten, nebst einem Beitrag zur Sauerstoffkatalyse der schwefligen Säure*, Göttingen, 1895 ; A. Hantzsch, *Zeit. phys. Chem.*, **72**. 362, 1910 ; V. K. la Mer and C. L. Read, *Journ. Amer. Chem. Soc.*, **52**. 3098, 1930 ; H. R. Moore and W. Blum, *Journ. Research Bur. Standards*, **5**. 255, 1930 ; W. V. Bhagwat and N. R. Dhar, *Journ. Indian Chem. Soc.*, **6**. 807, 1929 ; S. Takegami, *Bull. Japan. Chem. Soc.*, **5**. 16, 1930 ; N. Wertberg, *Tek. Tids.*, **59**. 41, 1929.

[8] H. Moissan, *Le chrome et ses composés*, Paris, 1884 ; J. M. Eder, *Monatsh.*, **12**. 1300, 1656, 1879 ; *Zeit. Physik*, **37**. 235, 1926 ; *Journ. prakt. Chem.*, (2), **19**. 294, 1879 ; *Ueber die Reactionen der Chromsäure und der Chromate auf Gelatine, Gummi, Zucker und andere Substanzen organischen Ursprungs in ihren Beziehungen zur Chromephotographie*, Wien, 1878 ; M. Ponton, *Edin. Phil. Journ.*, **27**. 169, 1839 ; E. Kopp, *Chem. Centrb.*, (1), **17**. 383, 1865 ; W. H. F. Talbot, *Compt. Rend.*, **36**. 780, 1843 ; *Journ. Photogr. Soc.*, **1**. 42, 62, 1854 ; A. Poitevin, *ib.*, **42**. 20, 1856 ; **52**. 95, 1861 ; **62**. 95, 1866 ; J. C. Schnauss, *Arch. Pharm.*, (3), **2**. 41, 1873 ; T. Swensson, *Zeit. phys. Chem.*, **91**. 624, 1916 ; H. Zocher and K. Coper, *ib.*, **132**. 302, 1928 ; E. Goldberg, *Beiträge zur Kinetik photochemischer Reaktionen*, Leipzig, 1906 ; R. Luther and G. S. Forbes, *Journ. Amer. Chem. Soc.*, **31**. 770, 1909 ; G. S. Forbes, J. C. Woodhouse and R. S. Dean, *ib.*, **45**. 1891, 1923 ; G. S. Forbes and P. A. Leighton, *Journ. Phys. Chem.*, **30**. 1628, 1926 ; J. Plotnikoff and M. Karsulin, *Zeit. Physik*, **36**. 277, 1926 ; **38**. 532, 1926 ; J. Plotnikoff, *Allgemeine Photochemie*, 215, 416, 583, 1890 ; *Bull. Acad. Russ.*, 1093, 1919 ; *Chem. Ztg.*, **52**. 669, 1928 ; *Zeit. wiss. Photochem.*, **19**. 22, 1919 ; H. C. Winther, *ib.*, **9**. 229, 1911 ; F. Weigert, *Zeit. phys. Chem.*, **101**. 414, 1922 ; M. Schiel, *Atelier Phot.*, **33**. 26, 1926 ; J. Krämer, *ib.*, **34**. 70, 1927 ; F. Schömmer, *Phot. Rund.*, **63**. 120, 138, 1926 ; A. Popovicky, *Journ. Russ. Phys. Chem. Soc.*, **55**. 1, 1924 ; E. J. Bowen and C. W. Bunn, *Journ. Chem. Soc.*, 2353, 1927 ; R. E. Liesegang, *Phot. Korr.*, **62**. 77, 1926 ; B. K. Mukerji and N. R. Dhar, *Journ. Phys. Chem.*, **32**. 1308, 1928 ; *Journ. Indian Chem. Soc.*, **5**. 411, 1928 ; E. Müller, *Zeit. Elektrochem.*, **32**. 399, 1926 ; J. E. Liebreich, *ib.*, **27**. 94, 452, 1921 ; **29**. 208, 1923 ; **30**. 186, 1924 ; A. Kleffner, *ib.*, **29**. 488, 1923 ; K. Oyabu, *ib.*, **29**. 491, 1923 ; G. J. Sargeant, *Trans. Amer. Electrochem. Soc.*, **37**. 479, 1920 ; A. V. Pamfiloff, *Bull. Inst. Polyt. Ivanovo-Voznesensk*, **4**. 113, 1921 ; D. J. MacNaughtan and R. A. F. Hammond, *Trans. Faraday Soc.*, **26**. 481, 1930.

[9] K. Honda and T. Sone, *Science Rep. Tohoku Univ.*, **3**. 223, 1914 ; E. Wedekind and C. Horst, *Ber.*, **48**. 105, 1915 ; L. Blanc, *Ann. Chim. Phys.*, (10), **6**. 182, 1926 ; P. Pascal, *Compt. Rend.*, **147**. 242, 742, 1908 ; L. A. Welo, *Phil. Mag.*, (7), **6**. 481, 1928.

§ 14. The Chemical Properties of Chromium Trioxide

According to J. J. Berzelius,[1] and O. Unverdorben, chromium trioxide has no smell; it tastes first acidic, then harsh, but not metallic; and it stains the skin yellow—the stain is not removed by water but it is removed by alkalies. Chromium trioxide solid or in aq. soln., or in sulphuric acid soln., or in the form of its salts, is a strong oxidizing agent, and is therefore reduced by many agents. E. Ludwig observed that **hydrogen** quickly reduces a conc. soln. of chromium trioxide, but acts only slowly on a dil. soln. W. N. Ipatieff and co-workers found that an acidic neutral or alkaline soln. of chromium trioxide at 280° to 300° is reduced by hydrogen under a press. of 200 atm. to form crystals of $Cr_2O_3.H_2O$. In the presence of free sulphuric acid at 300° and 80 atm., small violet-grey crystals, soluble in neither acid nor alkali, are formed and, in the latter case, appear to have the composition $R_2O.2Cr_2O_3.3SO_3.H_2O$. At 280° and 150 to 200 atm., the compound $2Cr_2O_3.3SO_3.6H_2O$ is obtained as dark green, cubic crystals. In the presence of ferrous or ferric sulphate, complex isomorphous mixtures containing iron and chromium are obtained in the form of dark green, cubic crystals. Iron pyrites frequently accompanies such mixtures—*vide supra*, chromic oxyhydroxide. C. L. Reese observed that in the absence of a catalytic agent, a soln. of chromic acid, alone or in the presence of 1 to 15 per cent. by vol. of sulphuric acid, is not reduced by hydrogen below 50°; and only very slowly below 100°. After 116 hrs.' exposure, at 100°, 70 per cent. of hydrogen is oxidized; and at 156°, with 7 hrs.' exposure, 11 per cent. of hydrogen is oxidized and much oxygen is evolved owing to the decomposition of the chromic acid. The oxidation is not dependent on the thermal decomposition of chromic acid because it occurs at a temp. below that at which oxygen is evolved. An aq. soln. of chromic acid is not reduced by the hydrogen evolved by passing an electric current through the liquid, but if a trace of sulphuric acid or a sulphate be present, reduction occurs until a certain limit is reached, and this is dependent on the conc. of the acid. A. C. Chapman found that acidic soln. of chromates are reduced to chromic salts by hydrogenized palladium. J. Hargreaves and T. Robinson observed the reduction of chromates to chromic oxide when heated in hydrogen. Purified chromium trioxide exposed to **air** slowly becomes moist, and deliquescent. A. Mailfert found that in the presence of ether, **ozone** furnishes perchromic acid; but H. Moissan could not obtain blue perchromic acid by the action of ozone on a soln. of chromic acid. Chromium trioxide was found by H. Rose to dissolve in a small proportion of **water** forming a dark reddish-brown soln., and with a larger proportion of water, the colour is lemon-yellow. The aq. soln. reddens litmus. For the solubility in water, *vide supra*. According to M. Traube, in acidic soln., chromium trioxide is reduced by **hydrogen dioxide** to chromic oxide: $4CrO_3+8H_2O_2+6H_2SO_4=2Cr_2(SO_4)_3+7O_2+14H_2O$. L. C. A. Barreswil observed that a transient blue colour is produced before the evolution of oxygen begins—*vide infra*, perchromic acid. The reaction was discussed by A. Bach, E. Spitalsky, A. von Kess and F. E. Lederer, E. Spitalsky and N. Koboseff, and E. H. Riesenfeld and A. Wesch. The catalytic decomposition of potassium dichromate and hydrogen dioxide by cobalt salts is represented: $K_2Cr_2O_7+H_2O_2=2KCrO_4+H_2O$, and $2KCrO_4+H_2O_2=K_2Cr_2O_7+H_2O+O_2$. The velocity of the reaction is promoted by copper, manganese, nickel, and cerium salts. In that case, the reaction $2KCrO_4+H_2O_2=K_2Cr_2O_7+H_2O+O_2$ then gives way to the rapid reaction $2KCrO_4+CoCl_2+2H_2O=H_2CoO_3+K_2Cr_2O_7+2HCl$, and $H_2CoO_3+H_2O_2+2HCl=CoCl_2+3H_2O+O_2$, in agreement with the observation that a definite $H^{\cdot}$-ion conc. is necessary for the promotion. This explanation agrees with the observation that a definite hydrogen-ion conc. is necessary for the promotion. Oxidation of the cobalt is indicated by a decrease in the conc. of the perchromic acid in the promoted reaction. The cobalt may be in the ter- or quadri-valent state during the promotion. The catalytic decomposition of hydrogen dioxide by potassium dichromate was studied by E. Spitalsky and N. Koboseff; and its acceleration by manganese salts by

A. C. Robertson. According to E. Spitalsky and N. Koboseff, during the catalysis of hydrogen dioxide by chromic acid or by acidified soln. of potassium dichromate the conductivity at first decreases sharply to a value which remains approximately constant during the major part of the reaction and then returns to its initial value as the reaction approaches completion. These changes are due to the formation and decomposition of catalytic intermediate compounds, and are, as is the catalysis itself, completely reversible, so that for each initial conc. of the substrate a definite value is obtained for the conductivity decrease and for the minimum conductivity. That the conductivity changes afford a parallel with the complicated kinetics of the reaction in dil. acid soln. is indicated by the coincidence of the maxima of the velocity of catalysis and of the velocity of the conductivity change. From the decrease of the conductivity the extent to which the hydrogen ions are used up in the formation of intermediate compounds may be calculated; the flat portion of the velocity curves represents the complete removal of the hydrogen ions, whilst the velocity maximum expresses their liberation near the end of the reaction. The relationships have been determined at constant substrate conc. of the reaction velocity and of the conductivity decrease with (1) variation of the dichromate conc. at constant acid conc.; (2) variation of the acid conc. at constant dichromate conc.; and (3) variation in constant ratio of both the acid and dichromate conc. In the third case only the reaction velocity and the conductivity decrease are influenced in the same manner by the conc. changes. The nature of the curves obtained leads to the hypothesis that during the course of the reaction two intermediate compounds, M_1 and M_2, are formed reversibly, which require no hydrogen ions for their formation and possess relatively small affinity constants, together with a third compound M_3, which is much more stable and requires hydrogen ions for its formation. From the initial acid and dichromate concentrations and the decrease of hydrogen-ion conc. during the catalysis the most probable nature of the more stable compound M_3 is given by the equation: $2Cr_2O_7''+2H_2O_2+K^{\cdot}+H^{\cdot}=KH_5Cr_4O_{18}''$, the affinity constant of the reaction being 10^{13}. The velocity constants $k_1=42$, and $k_2=5{\cdot}6$. On the flat portion of the velocity curve, where, at high concentrations of hydrogen peroxide, the more stable additive compound M_3 is but little dissociated, the catalysis is effected simultaneously by two intermediate compounds, viz., M_3 and the compound M_1, which is the active agent in the catalysis in neutral soln. Towards the end of the reaction, as the hydrogen peroxide conc. becomes very small, M_3 decomposes and releases the hydrogen ions; very active but short-lived intermediate compounds are then formed, and account for the sharp maximum in the reaction velocity. From the affinity constants of M_1 and M_3, bearing in mind the possible existence of another substance M_2, the reaction velocity curves agree fairly well with part of the experimental curves.

According to H. Moissan,[2] chromium trioxide does not react with **chlorine** free from hydrogen chloride; and K. H. Butler and D. McIntosh observed that the trioxide is insoluble in liquid chlorine, and has no effect on the b.p. of the liquid. According to A. Michael and A. Murphy, a soln. of chlorine in carbon tetrachloride in a sealed tube at 175° forms chromyl and carbonyl chlorides. H. Moissan observed that **bromine** has no action on the trioxide. I. Walz found that a conc. soln. of chromium trioxide, when poured on **iodine,** rapidly turns black and assumes a syrupy consistency, and the liquid thus formed does not respond to the tests for free iodic or hydriodic acid; chromium hypoiodite may be formed. A mixture of sulphuric acid and chromium trioxide oxidizes iodine to iodic acid. O. Ruff and H. Krug found that the trioxide is vigorously attacked by **chlorine trifluoride.** L. Henry showed that **hydrogen chloride** forms chromyl chloride: $CrO_3+2HCl=CrO_2Cl_2+H_2O$. The water so formed reacts with the chromyl chloride producing a dark oily liquid. W. Autenrieth added that the reaction with dry hydrogen chloride is vigorous and chromyl chloride is formed; with 35 to 40 per cent. **hydrochloric acid,** 35 per cent. of the acid forms chromyl chloride: $CrO_3+2HCl=CrO_2Cl_2+H_2O$; with 20 per cent. hydrochloric acid, chlorine, as well as chromyl chloride, is produced:

$2CrO_3+12HCl=2CrCl_3+3Cl_2+6H_2O$. F. Penny said that with boiling hydrochloric acid chromic chloride and chlorine are formed. J. W. Thomas found that hydrogen chloride reduces chromates and dichromates. R. J. Meyer and H. Best obtained chromyl chloride by the action of hydrogen chloride on an acetic acid soln. of chromium trioxide. H. Moissan found that dry **hydrogen bromide** does not act on chromium trioxide; while, according to F. Penny, boiling **hydrobromic acid** yields bromine. M. Bobtelsky and A. Rosenberg found that the velocity measurements agreed with the typical formula for a reaction of the second order; and the effects of salts on the speed of the reaction are summarized in Fig. 27. The action of the salts decreases in the order: $NiCl_2>MgCl_2>FeCl_3>HCl>AlCl_3>CrCl_3$; and $HgCl_2>CdCl_2>ZnCl_2$, where the action of the mercuric chloride is catalytic, and zinc chloride exerts a neutral salt effect. The subject was also discussed by M. Bobtelsky, and by M. Bobtelsky and D. Kaplan. L. L. de Koninck noticed that when potassium bromide is melted with a chromate, bromine is liberated.

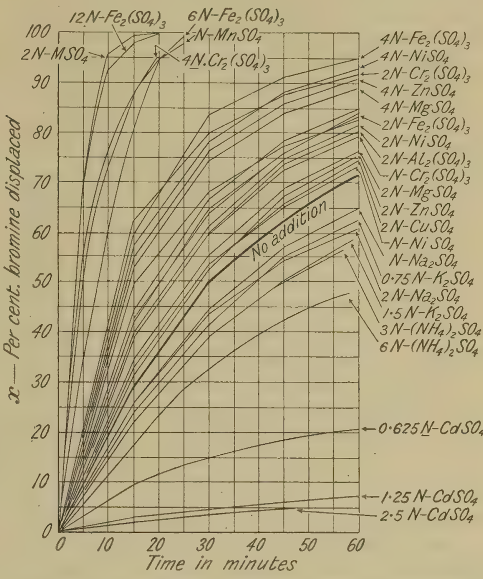


FIG. 27.—The Effect of Salts on the Reaction: $6HBr+2CrO_3=Cr_2O_3+3H_2O+3Br_2$.

H. Moissan found that dry **hydrogen iodide** has no action on chromium trioxide; and F. Penny, C. F. Mohr, E. Donath, and M. M. Richter observed that with boiling **hydriodic acid,** and iodides, iodine is set free. According to W. Ostwald, the reaction $2CrO_3+6HI=2Cr(OH)_3+3I_2$ is accelerated by the presence of free acids proportionally with the affinity constants of the acids. R. E. de Lury found that the velocity of oxidation of potassium iodide by potassium dichromate is proportional to the conc. of the dichromate, and to the square of the conc. of the acid employed. The temp. coeff. of the reaction is about 1·4. The presence of ferric salts strongly accelerates the reaction. The theory of R. Luther and co-workers is that the induction of the reaction between chromic acid and iodides by ferrous salts is due to the formation of quinquevalent chromium by the reaction between ferrous ions and sexivalent chromium ions, these then oxidizing other ferrous ions and also iodide ions. According to C. Wagner and W. Preiss, the equilibrium $Cr^{VI}+Fe^{II}\rightleftharpoons Cr^{V}+Fe^{III}$ is established very rapidly, and C. C. Benson, having shown that the oxidation of ferrous salts by chromic acid is proportional to the square of the conc. of the ferrous salt, said that the reaction between Cr^{V}-ions and $Fe^{\cdot\cdot}$-ions can primarily involve only one of the latter, somewhat as follows: $Cr^{V}+2Fe^{II}\rightarrow Cr^{III}+2Fe^{III}$. The reaction with the iodide ion also proceeds in two stages with hypoiodous acid as an intermediate product: $Cr^{V}+I^{I}+HO^{I}\rightarrow Cr^{III}+HIO$; and $HIO+H^{\cdot}+I'\rightarrow I_2+H_2O$. The values of the velocity cosntants indicate that there is a side reaction involving the splitting up of some Cr^{V}-ions possibly into Cr^{III}- and Cr^{VI}-ions. The reaction was also studied by K. Seubert and J. Carstens, K. Seubert and A. Henke, C. Wagner and W. Preiss, P. A. Meerburg, R. H. Clark, W. Manchot and R. Kraus, R. F. Beard and N. W. Taylor, W. Preiss, A. Schükareff, C. C. Benson, J. M. Bell, W. C. Bray, R. A. Gortner, R. Luther and T. F. Rutter, M. H. Golblum and L. Lew, M. Bobtelsky, and N. A. Orloff. W. B. Morehouse found the X-ray absorption of aq. soln. is greater by 0·25 per cent. after than before the reaction : $K_2Cr_2O_7+12KI+14HCl=8KCl+2CrCl_3+3I_2+6KI+7H_2O$. N. Schiloff studied the catalytic action of chromate ions on the reaction between potassium bromate and potassium iodide. N. R. Dhar showed that the speed of the reaction between chromic acid and potassium iodide is increased in sunlight ; and S. S. Bhatnagar and co-workers, that it is accelerated by a magnetic field. F. E. E. Germann and D. K. Shen studied the action of chromic acid on silver iodide photographic plates.

H. Moissan[3] found that when chromium trioxide is heated with **sulphur,** the mixture inflames, forming sulphur oxides and chromium sulphide. K. Brückner said that chromic oxide and a little sulphide are formed. J. B. Senderens observed that when the mixture is triturated in the cold, sulphur dioxide and a brown mush of chromic chromate and sulphate are formed—if water be present, the reaction does not occur in the cold. According to O. Harten, when **hydrogen sulphide** is passed over heated chromium trioxide, decomposition occurs with incandescence : $2CrO_3+6H_2S=Cr_2S_3+6H_2O+3S$. H. B. Dunnicliff and C. L. Soni studied the mechanism of the reaction, which they represented : $2H_2CrO_4+3H_2S=2Cr(OH)_3+2H_2O+3S$. H. Rose found that an aq. soln. of chromic acid reacts with hydrogen sulphide forming water, sulphur, and hydrated chromic oxide ; aq. soln. of chromates mixed with acid become green when treated with hydrogen sulphide, and sulphur is precipitated ; hot soln. are rapidly decomposed forming sulphuric acid. M. Traube found that dry **sulphur dioxide** does not react with dry chromium trioxide at 100°, and at 180°, sulphur trioxide and chromic chromate are slowly formed. P. Berthier said that aq. soln. of potassium dichromate and chromate are changed rapidly into a mixture of sulphate and dithionate ; with the chromate soln., brown chromium hydroxide is first formed and then dissolved as more sulphur dioxide is passed into the soln. According to H. Bassett, when potassium dichromate, potassium chromate, or chromic acid is reduced by sulphurous acid, 94 to 95 per cent. of sulphate is formed together with 5 to 6 per cent. of dithionate, the amount of the latter produced being independent of the temp. The freshly reduced soln. do not give the reactions of chromium or of SO_4-ions, and appear to contain a compound $(KSO_4)Cr_2(SO_4)_2(KSO_3)$, or the corresponding acid, which slowly decomposes into chromic sulphate and potassium sulphite. If sulphuric acid or potassium sulphate is added to these soln., the reactions of SO_4 are not given by the resulting mixture. It seems possible that one mol of chromium sulphate may mask the reaction of as many as six mols of sulphuric acid. A. Skrabal said that if chromic acid be rapidly reduced by sulphur dioxide an unstable, green chromic salt is formed ; and if slowly reduced with a feebly acid soln., a violet chromic salt is formed. H. Rose found that conc. **sulphuric acid** dissolves chromium trioxide forming, in the cold, a brownish-yellow soln. which gradually deposits crystals of chromium trioxide ; if the soln. is heated to the evaporation temp. of sulphuric acid, oxygen is evolved and chromic chromate and sulphate are formed. A. Wesch observed that when warmed with sulphuric acid, chromium trioxide is decomposed more turbulently than potassium dichromate—oxygen is evolved but no ozone. C. Weltzien, and C. T. Kingzett observed that when conc. sulphuric acid and potassium dichromate are heated together, ozonized oxygen is evolved ; J. C. G. de Marignac denied this. L. I. de N. Ilosva attributed the reaction to the presence of chlorine, not ozone, but R. Kraus found that when powdered potassium dichromate, free from chlorine is triturated with conc. sulphuric acid, ozone is formed. O. Brunck also observed a formation of ozone. A. W. Rakowsky and D. N. Tarassenkoff measured the solubility of chromium trioxide in sulphuric acid between 0° and 100°, and they said that the smooth curves with high concentrations of sulphur trioxide suggest the existence of only one solid phase. A. Schrötter, and P. A. Bolley observed the solubility of chromium trioxide in sulphuric acid respectively of sp. gr. 1·660 and 84·5 per cent. ; and J. Fritzsche found it to be very soluble in sulphuric acid of sp. gr. 1·85. L. F. Gilbert and co-workers found the solubility expressed in molar percentages at 25° to be :

SO_3 .	0	1·47	16·41	32·04	33·17	37·79	38·97	45·80	58·94
CrO_3 .	25·78	21·10	1·11	1·62	1·58	0·43	0·36	0·44	0·88
Solid phase	CrO_3				$CrO_3.SO_3$			$CrO_3.SO_3.H_2O$	

The results are plotted in Fig. 75, in connection with chromyl sulphate. The solubilities at 45° are:

SO_3	5·25	16·73	22·01	31·05	33·55	34·67	37·07	42·26	45·67
CrO_3	13·79	1·00	0·17	1·16	1·15	1·11	0·63	0·38	0·30
Solid phase	CrO_3				$CrO_3.SO_3$				$CrO_3SO_3.H_2O$

The results of A. W. Rakowsky and D. N. Tarassenkoff between 0° and 100°, are plotted in Fig. 28. The hydrate $SO_3.2H_2O$ forms metastable mixed crystals with chromium trioxide. J. Fritzsch said that the trioxide is slightly soluble in a soln. of **potassium hydrosulphate.** According to O. Brunck, chromium trioxide and chromates are immediately reduced by **sodium hyposulphite** at ordinary temp. forming chromic oxide or chromic salts. A. Longi and L. Bonavia observed that in the reaction between chromium trioxide and **thiosulphates,** W. Diehl's equation: $4K_2Cr_2O_7 + 3Na_2S_2O_3 + 13H_2SO_4 = 3Na_2SO_4 + 4Cr_2(SO_4)_3 + 4K_2SO_4 + 13H_2O$ is not correct. On adding a mineral acid and potassium dichromate to a dil. soln. of sodium thiosulphate, A. Longi found that the reaction: $2H_2CrO_4 + 6H_2S_2O_3 = 3H_2S_4O_6 + 2Cr(OH)_3 + 2H_2O$, occurs; small quantities of sulphuric acid are simultaneously formed in accordance with the secondary reaction: $3H_2S_4O_6 + 14H_2CrO_4 + 16H_2O = 12H_2SO_4 + 7Cr_2(OH)_6$. Hydrogen sulphide is also produced, and both sodium thiosulphate and tetrathionic acid give this gas when small quantities of an acid or a chromic salt are added to their soln.; more hydrogen sulphide is obtained at high than at low temp., and tetrathionic acid is more stable than the thiosulphate, for sodium thiosulphate gives hydrogen sulphide when treated with hydrogen dioxide or acetic acid, or when carbon dioxide is passed through its hot soln. The reaction was studied by F. J. Faktor; and G. Powarnin and M. Chitrin showed that in conc. soln., the oxidation proceeds most readily in the absence of an excess of acid—*i.e.* no more than $8H^{\cdot}$ per 2Cr. No more than 4·2 mols of thiosulphate per mol of potassium dichromate take part in the first stage of the reaction; the proportion of sulphur separated increases with the conc. of the $H^{\cdot}$-ions; in neutral soln. no sulphur is formed and the reaction proceeds: $2Cr_2O_7'' + S_2O_3'' = CrO_4'' + 2SO_3'' + 3CrO_2$. When the proportion of $H^{\cdot}$-ions is raised from 8 to 14 per 2Cr, the amount of thiosulphate which undergoes change is altered, and more sulphur is separated. This indicates that when the conc. of the $H^{\cdot}$-ions is low, tetrathionate is formed, and the tetrathionate is decomposed when the conc. of the $H^{\cdot}$-ions is high. H. Moissan observed that **selenium** reacts violently with the trioxide.

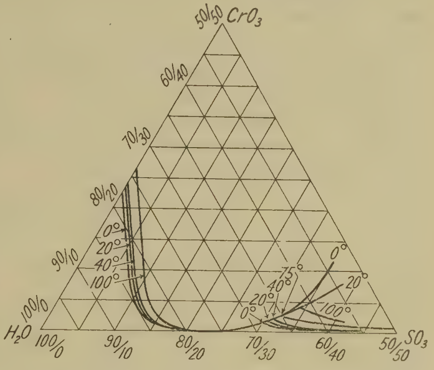


FIG. 28.—The Ternary System: CrO_3–SO_3–H_2O between 0° and 100°.

H. Moissan [4] said that **nitrogen** has no action on chromium trioxide. O. Unverdorben, and R. Böttger showed that **ammonia** gas decomposes the dry trioxide with incandescence at ordinary temp. forming chromic oxide. M. Berthelot examined the heat of the reaction. E. C. Franklin said that the trioxide is slightly soluble in liquid ammonia. According to A. Rosenheim and F. Jacobsohn, liquid ammonia acts on chromium trioxide in a sealed tube at ordinary temp. forming a brown complex-chromium triamminotrioxide, $CrO_3.3NH_3$, or more probably ammonium imidochromate, $NH : CrO(O.NH_4)_2$—*vide* amido compounds, **8**. 49, 21.

For the action of aq. ammonia, *vide* the ammonium chromates. F. Ephraim observed that the trioxide reacts vigorously when triturated with **sodium amide.** T. Curtius and F. Schrader observed that **hydrazine** is decomposed explosively by chromates; U. Roberts and F. Roncali said that 2 mols of potassium dichromate develop 3 mols of nitrogen, while K. Seubert and J. Carstens represented the reaction: $H_2Cr_2O_7+N_2H_4=2CrO_2+3H_2O+N_2$—chromium dioxide is formed as an intermediate product. E. J. Cuy and W. C. Bray represented the reaction with hydrazine in acidic soln. by $3N_2H_5{}^{\cdot}+2Cr_2O_7{}''+13H^{\cdot}=3N_2+4Cr^{\cdot\cdot\cdot}+14H_2O$. E. Schweizer represented the reaction in aq. soln. with **nitric oxide** by: $2K_2Cr_2O_7+2NO=2KNO_3+K_2CrO_4+Cr_2O_3.CrO_3$. The reaction was also studied by H. Reinsch, and C. W. Eliot and F. H. Storer. P. Grouvelle, and F. Wöhler found that **nitrous acid** reduces chromium trioxide in aq. soln. H. Rose said that **nitric acid** does not change the chromic acid of the chromates, but in conc. soln. red fuming nitric acid reduces chromic acid to chromic oxide and brown chromic chromate. E. Zettnow said that chromic acid is insoluble in nitric acid of greater sp. gr. than 1·46; and R. Bunsen, in fuming nitric acid containing no nitrous oxides. S. A. Mumford and L. F. Gilbert found that the solubilities of chromic acid in nitric acid of different conc., when compositions are expressed in grams per 100 grms. of soln., are, at 25°,

HNO_3 .	0	2·28	5·95	13·25	35·35	59·11	74·47	82·90	91·36
CrO_3 .	62·85	60·31	56·47	48·10	25·54	4·88	0·27	0·06	8·29

there is a minimum at 0·06 per cent. CrO_3. At 45°, there is a minimum with 0·44 per cent. CrO_3:

HNO_3 .	0	2·05	5·58	19·53	50·69	73·81	81·55	91·83	98·06
CrO_3 .	53·51	61·27	57·93	43·41	13·15	0·88	0·44	3·39	9·42

The minimum solubility occurs with nitric acid approximating $18N$-HNO_3, or $HNO_3.H_2O$. The curves are simple and continuous. The sp. gr. of the mixed soln. are only approximately additive. H. Moissan observed that **phosphorus** reacts explosively with molten chromium trioxide; and A. Oppenheim found that an aq. soln. of chromic acid at 200° is reduced by red phosphorus to chromic chromate. According to J. Jacobson, phosphorus dissolves in a soln. of chromic acid to form chromic phosphate. E. Kopp observed that a soln. of potassium dichromate when heated, or exposed to sunlight, is reduced by phosphorus. Observations on this subject were made by A. Stiassny, and J. W. Slater—*vide* phosphorus. According to G. Viard, the rate of the reaction between chromic acid and **phosphorous acid** can be represented by $dx/dt=k(a-x)^4$. The initial velocity varies according to a 1·4 power of the concentration. S. S. Bhatnagar and co-workers found that the reduction with phosphorous acid is accelerated by a magnetic field. A. D. Mitchell represented the reaction with **hypophosphorous acid** (*q.v.*): $H_3PO_2+Cr_2O_7{}''=H_3PO_3+Cr_2O_6{}''$; followed by $2H_3PO_2+Cr_2O_6{}''+8H^{\cdot}=2H_3PO_3+2Cr^{\cdot\cdot\cdot}+4H_2O$. *Vide infra*, for the phosphochromates formed by condensation with **phosphoric acid.** H. Schiff represented the reaction with **phosphorus pentachloride** by $CrO_3+PCl_5=CrO_2Cl_2+POCl_3$, and by a secondary reaction, chromic chloride is formed. P. Walden showed that chromium trioxide is virtually insoluble in **phosphoryl chloride.** H. Moissan found that **arsenic** reacts with chromium trioxide with incandescence, forming arsenide. According to C. Reichard, an aq. soln. of chromium trioxide is reduced by **arsenic trioxide**; and the reaction was studied by R. E. de Lury, and W. L. Miller. A. Skrabal showed that if the reaction proceeds slowly, violet chromic salt is formed, and if rapidly, a green salt—*vide* **9**. 51, 22, for the arsenic chromates formed by condensation with **arsenic acid.**

M. Berthelot [5] found that when heated with conc. chromic acid, **carbon** furnishes carbon dioxide and oxalic acid. E. B. Alekseevsky and A. P. Musakin studied adsorption of chromic acid by charcoal. J. Hargreaves and T. Robinson noted that alkali chromates are reduced to chromic oxide by **carbon monoxide,** and an alkali carbonate is formed. B. Neumann and C. Exssner studied the conversion of soln.

of sodium chromate to dichromate by **carbon dioxide** under press. H. E. Armstrong observed that with **carbon disulphide** at 180°, a little carbonyl sulphide is formed; and R. Böttger observed that heated chromium trioxide is reduced by carbon disulphide. I. Guareschi found that **cyanogen bromide** is decomposed by chromic acid, forming bromine, chromic oxide, carbon dioxide, and ammonia. K. Someya studied the electrometric titration of potassium dichromate and potassium ferrocyanide. E. Ludwig observed that **methane** is not attacked by chromium trioxide; while **ethylene** furnishes carbon dioxide, water, formic acid, probably acetic acid, and, according to M. Berthelot, some aldehyde. M. Berthelot also observed that with **acetylene,** a conc. soln. of chromic acid gives carbon dioxide and formic acid, while with dil. soln. some acetic acid is formed; **allylene** yields propionic and acetic acids, etc.; and **propylene,** propionic acid, acetone, etc. R. Fittig found that the side-chains of the **aromatic hydrocarbons** are oxidized to CO.OH groups by chromic acid or a mixture of sulphuric acid and potassium dichromate. According to A. Schafarik, commercial **benzene** inflames in contact with powdered chromium trioxide, but **petroleum,** rectified over sodium, shows scarcely any signs of action after some weeks' contact with chromium trioxide; R. Böttger observed that the heated trioxide is reduced by petroleum or **turpentine.** A. Gawalowsky said that while chromium trioxide and chromates oxidize **alcohol** to aldehyde, a highly purified aq. soln. of chromic acid does not act on alcohol, but it does so if a drop of sulphuric acid be added. J. M. Eder added that a soln. of ammonium dichromate in absolute alcohol decomposes more rapidly than a soln. in 50 per cent. alcohol. The reaction is favoured by light. E. J. Bowen and C. W. Bunn studied the photochemical oxidation of the alcohols—methyl, ethyl, *n*-propyl, and *iso*-propyl—by dichromates. H. Wienhaus observed that chromic esters can be obtained by shaking a soln. of an aromatic tertiary alcohol in light petroleum or carbon tetrachloride with an excess of chromium trioxide. Aromatic secondary alcohols were decomposed by treatment with chromic acid; thymol was coloured blue; and eugenol was oxidized without coloration. S. Takegami observed that colloidal chromic chromate, $Cr(CrO_4)_3$, is formed when alcohol is added to a soln. of chromic acid. E. Müller and co-workers also studied the reaction. B. V. Tronoff and co-workers studied the velocity of oxidation of alcohol; and D. S. Morton examined the photochemistry of the reaction. A. Schafarik said that chromium trioxide is soluble in dried **ether,** freed from alcohol. R. M. Isham and C. E. Vail said that when chromic acid is added to ether, a violent reaction takes place with evolution of acetaldehyde vapour and the separation of green chromic oxide. If the chromic acid is introduced into ether previously cooled to −10°, a yellow soln. is first produced, but oxidation begins almost immediately with the same results as those obtained at the ordinary temp. B. V. Tronoff studied the velocity of oxidation of ethers and **esters.** A. Naumann said that the trioxide is soluble in **acetone.** N. R. Dhar, and G. Ulrich and T. Schmidt studied the reducing action of **formic acid** on chromium trioxide. C. Wagner observed that the reaction with formic acid progresses in stages, $CrO_3 \rightarrow Cr^V \rightarrow Cr^{III}$; and if a manganous salt is present as negative catalyst, $CrO_3 \rightarrow Cr^V \rightarrow 2Cr^{II} + Cr^{III}$. The retarding action of manganous salts on the oxidation of formic or lactic acid by chromic oxide is ascribed to their promoting the transformation of the quinquevalent chromium into sexivalent and tervalent chromium. A. Pictet found that glacial **acetic acid** forms acetochromic acid, $HO.CrO_2.C_2H_3O_2$; and A. Pictet and P. Genequand could not prepare a similar compound with formic acid or with **valeric acid** because of their reducing action; but with **butyric acid,** butyrochromic acid, $HO.CrO_2.C_4H_7O_2$, is formed. The oxidation of **oxalic acid** by chromium trioxide was observed by H. Vohl, W. P. Jorissen and L. T. Reicher, B. K. Mukerji and co-workers, A. K. Bhattacharya and N. R. Dhar, H. Kunz-Krause and P. Manicke, N. R. Dhar, and M. Prud'homme. K. Jablczynsky deduced an equation for the reducing action of oxalic acid on the assumption that it occurs in three stages; $Cr^{VI} \rightarrow Cr^V$ (i), $Cr^V \rightarrow Cr^{IV}$ (ii), and $Cr^{IV} \rightarrow Cr^{III}$ (iii). The velocity constants are respectively k_1=0·0344, k_2=0·1322, and k_3=0·0238. N. R. Dhar found the reaction is about four times as fast in tropical sunlight as in darkness. The reaction was also studied by A. K. Bhattacharya and N. R. Dhar. C. Wagner observed that if a soln. of chromic acid is added to a mixed soln. of potassium iodide and sodium hydrocarbonate, no free iodine is formed, but a reacting mixture of oxalic and chromic acids will liberate appreciable amounts of iodine from the iodide. It is therefore to be concluded that some active intermediate product is formed in the reaction between chromic acid and oxalic acid, and the same is true for the reaction between chromic acid and tartaric acid. This substance is so unstable that it can scarcely be hydrogen peroxide, or a compound, of the nature of percarbonic acid, and attempts to detect the formation of these substances have, in fact, been futile, nor is there any evidence in favour of the existence of chromic acid-oxalic acid complexes. In the reaction between chromic acid and lactic acid, however, the intermediate product is more stable, probably owing to the formation of a complex compound with the lactic acid. Intermediate products are also formed in the oxidation of oxalic, **lactic, tartaric, and thiocyanic acids** by chromic trioxide. Chromium trioxide decomposes tartaric acid, and **citric acid** as observed by W. P. Jorissen and L. T. Reicher, and W. G. Vannoy. A. K. Bhattacharya and N. R. Dhar studied the photochemical decomposition of citric, tartaric, and lactic acids by chromic acid. H. S. Fry found chromium trioxide to be soluble in **acetic anhydride ;** and that **acetyl chloride** dissolved in carbon tetrachloride forms chromyl chloride ; **acetyl bromide** forms chromyl bromide ; but **acetyl iodide** does not react. A. Naumann observed that chromium trioxide is soluble in **benzonitrile,** and in **methyl acetate ;** but is sparingly soluble in **ethyl acetate.** R. Böttger found that ethyl acetate, and **ethyl nitrate** reduce hot chromium trioxide to chromic oxide. M. Prud'homme showed that the oxidation of indigo is greatly accelerated by the presence of oxalic acid. The reducing action of **paper** was observed by A. Maus ; **wool,** by G. Ulrich and T. Schmidt ; **sugar,** by W. P. Jorissen and L. T. Reicher ; **vegetable products,** by J. Jacobson ; **gelatin,** by E. P. Wightman and S. E. Sheppard ; and **animal fibres,** by M. A. Ilinsky and D. I. Kodner. E. Goldberg found that the velocity of the reaction with **quinine** in light is proportional to the intensity of light ; only those rays are active which are absorbed ; Beer's law holds good ; and the temp. coeff. of the reaction is small. R. Luther and G. S. Forbes showed that the quinine is alone sensitive to the light so that the first stage of the reaction is the formation of sensitized quinine with a velocity proportional to the light absorption ; and the second stage is a reaction with the sensitized quinine with a velocity which is proportional to the conc. of the chromic and sulphuric acids. The reaction was studied by D. S. Morton. A. K. Bhattacharya and N. R. Dhar, and B. K. Mukerji and co-workers studied the reaction with quinine sulphate. L. Cohn, and A. Windhaus indicated the use of chromium trioxide in the oxidation of organic compounds in the laboratory, and A. N. Dey and N. R. Dhar studied the kinetics of the oxidation of organic acids by chromic acid. Chromic acid and soluble chromates give precipitates with basic dyes, but not so with the insoluble chromates.

According to P. Lebeau,[6] **silicon** is not attacked by chromium trioxide. R. Bunsen said that chromates heated before the blowpipe flame impart a green colour to beads from **borax,** or **microcosmic salt ;** and L. Möser and W. Eidmann, that **boron nitride** reduces the trioxide to a lower oxide. L. F. Gilbert studied the system CrO_3–B_2O_3–H_2O at 25° and 45°. For the solubility of **boric acid** and chromic acid in grams per 100 grms. of soln., and the sp. gr., he found :

25°	CrO_3 .	62·40	59·90	43·80	33·05	18·07	9·42	4·90
	B_2O_3 .	0·10	0·16	0·65	1·02	1·58	2·28	2·79
	Sp. gr. .	1·699	1·657	1·420	1·296	1·156	1·086	1·052
45°	CrO_3 .	61·56	58·10	57·50	57·34	53·80	25·60	2·40
	B_2O_3 .	0·90	0·92	0·87	0·12	0·85	2·33	4·76
	Sp. gr. .	1·674	1·612	1·603	1·603	1·528	1·219	1·038

J. L. Gay Lussac and L. J. Thénard observed that **sodium** or **potassium** reacts with chromium trioxide with incandescence. R. G. van Name and D. U. Hill found that the values for the monomolecular velocity constant k, in $dx/dt=k(a-x)$, when **copper** dissolves in 0·015 molar soln. of chromium trioxide with 0·05, 0·25, 1·25, and 5·0 molar proportions of sulphuric acid, were, respectively, 5·58, 6·95, 5·34, and 2·072; **silver** and the 0·015 molar chromium trioxide with 0·25, and 5·0 molar H_2SO_4, gave the constants 4·31, and 1·23 respectively. The initial velocity of the dissolution of silver in chromic acid is greater than that which characterizes the normal process of dissolution. This indicates that the velocity depends on the physical state of the metal, and is not entirely determined by the process of diffusion. The reduction of chromic acid by copper was discussed by V. H. Veley,[7] E. Murmann, and F. Fischer. According to R. G. van Name and D. U. Hill, in the action of $0·015M$-CrO_3 and $5·0M$-H_2SO_4 on **tin,** the velocity constant was 2·74; with **nickel,** 2·67; while with **cadmium** and $0·015M$-CrO_3 and 0·25, 1·25, and $5·0M$-H_2SO_4, the velocity constants were, respectively, 7·02, 5·32, and 2·67; and with **iron** and $0·015M$-CrO_3 with 0·25 and $5·0M$-H_2SO_4, the velocity constants were, respectively, 11·68, and 4·20. H. Moissan found that **zinc** reduces chromium trioxide and chromates to chromic oxide or salts; iron also reacts with the evolution of much heat. E. Heyn and O. Bauer observed that iron dissolves in dil. chromic acid, and iron treated with a certain conc. of the chromic acid, may be partially protected from rusting. R. G. van Name and D. U. Hill studied the rate of dissolution of copper, silver, cadmium, tin, and nickel in chromic acid. J. F. John found that **manganese** dissolves in chromic acid. J. Jacobson observed that **mercury** reduces an aq. soln. of chromium trioxide; and also soln. of chromates and dichromates. A. Charriou studied the adsorption of chromic acid by **aluminium hydroxide.** According to A. Scheurer-Kestner, **stannous chloride** is oxidized by chromium trioxide: $6SnCl_2+4CrO_3=3SnCl_4+3SnO_2+2Cr_2O_3$; F. Penny found that dichromates are also reduced by stannous chloride. M. Neidle and J. C. Witt found that the stoichiometric relations in the reaction between stannous chloride and potassium dichromate are the same in the absence of acid as in its presence; when potassium dichromate is added in the theoretical quantity to a soln. of stannous chloride in the absence of acid, brownish- and greenish-blue, gelatinous masses are formed, which dissolve and form a clear, deep olive-green soln. when the whole of the dichromate has been added. These soln. appear red by transmitted light. Dialysis, and extraction with alcohol, showed that the soln. consists of potassium and chromium chlorides, together with colloidal soln. of hydrated stannic and chromic hydroxides. On dialysis a clear sol, of the approximate composition $6SnO_2:1Cr_2O_3$, is obtained, and this sol contains the whole of the tin and about one-half of the chromium used in the reaction. The course of the reaction is given by the equation: $2K_2Cr_2O_7+6SnCl_4+(6x+y+1)H_2O \rightleftharpoons 4KCl+6SnO_2.xH_2O+Cr_2O_3.yH_2O+2CrCl_3+2HCl$. R. Kraus studied the action of soln. of **uranous salts** and **molybdous salts** on chromium trioxide soln.; and K. Someya, soln. of **titanous salts.** A. Geuther represented the reaction with anhydrous **ferric chloride** by: $2FeCl_3+3CrO_3=Fe_2O_3+3CrO_2Cl_2$. S. Orlowsky found that, in alkaline soln., potassium dichromate oxidizes **manganous salts** to manganic: $K_2Cr_2O_7+6MnSO_4+10NH_4OH+7H_2O=2Cr(OH)_3+6Mn(OH)_3+K_2SO_4+5(NH_4)_2SO_4$, and the more conc. the alkali, the smaller the oxidation produced. The reaction was studied by R. Lang and co-workers. For the action on permanganates, *vide* permanganates. Chromium trioxide is reduced by **ferrous salts.** M. Neidle and J. C. Witt found that the stoichiometric relations in the reaction between potassium dichromate and ferrous sulphate are the same in the presence or absence of acid. In the absence of acid the reaction is instantaneous, except in very dil. soln. The reaction may be expressed by the equation: $3K_2Cr_2O_7+18FeSO_4+(x+6y)H_2O=3K_2SO_4+Cr_2O_3.xH_2O+2Cr_2(SO_4)_3+3Fe_2(SO_4)_3+6(Fe_2O_3.yH_2O)$. The colloidal chromic and ferric oxides are precipitated by the sulphate ion in the soln., and adsorb a large quantity of ferric sulphate and smaller quantities of the other two sulphates. The electrometric titration of ferrous salts with potassium dichromate was studied by R. G. van Name and F. Fenwick, and E. Müller and H. Kogert. C. Rube observed that **potassium ferrocyanide** is converted into ferricyanide.

F. Penny, H. Schwarz, and J. Schabus found that a soln. of **ferrous sulphate** gives a yellowish-brown precipitate with chromates or dichromates, which ultimately dissolves and a green soln. of a chromic salt remains. C. C. Benson observed that the rate of oxidation of ferrous sulphate is proportional to the second power of the conc. of ferrous salt and of acid ; and approximately proportional to the 1·7 power of the conc. of the potassium dichromate. The presence of ferric salts retards the reaction. In the presence of iodide, the rate of oxidation of the ferrous salt is proportional to the conc. of the dichromate and ferrous sulphate, and to the third or fourth power of the conc. of the acid. Increasing the conc. of iodide causes at first a decrease and later an increase of the rate. The results are not in accord with the peroxide theory of W. Manchot, which assumes the primary product of oxidation of the ferrous sulphate to be a peroxide, which then reacts with the iodide and the remaining ferrous salt ; but they agree with the assumption that the iodide takes part in the reaction, and the two reactions are suggested as occurring together (i) between Cr_2O_7'', FeI', I', and $4H^{\cdot}$, and (ii) between Cr_2O_7'', $2Fe''$, and $2H^{\cdot}$. The reaction was discussed by W. L. Miller, and R. A. Gortner. The reaction between chromic acid and hydriodic acid in dil. soln. has been studied by N. Schiloff, R. Luther and N. Schiloff, and R. Luther and T. F. Rutter in the presence of hydriodic acid as acceptor, and vanadium salts as inductors. Bi-, ter-, and quadrivalent salts of vanadium are ultimately oxidized to quinquevalent vanadium. The inductor factor is 2, meaning that for one eq. of vanadium oxidized, two eq. of iodine are set free. Vanadic acid does not effect the rate of oxidation of hydriodic acid by chromic acid, and only acts comparatively slowly on hydriodic acid, so that the process is not greatly complicated by side reactions. With uranous sulphate as inductor, and a large excess of potassium iodide, the induction factor is 0·74. While W. Manchot supposed that the inductor is oxidized by chromic acid to a peroxide, R. Luther and T. F. Rutter assumed that the inductor reduces chromic acid to quinquevalent chromium, which is a more rapid oxidizing agent than the acid itself. Whereas W. Manchot's theory requires the formation of intermediate peroxides of very diverse formulæ, the assumption of the intermediate formation of quinquevalent chromium alone accounts for nearly all the reactions so far investigated. It is suggested that the reduction of chromic acid proceeds in the following stages $Cr^{VI} \rightarrow Cr^{V} \rightarrow Cr^{IV} \rightarrow Cr^{III}$, and that chromic acid contains sexivalent and not quadrivalent chromium as W. Manchot has suggested. N. R. Dhar studied some induced reactions, *e.g.* the action of chromic acid on the reduction of mercuric chloride by oxalic acid.

REFERENCES.

[1] J. J. Berzelius, *Schweigger's Journ.*, **22**. 53, 1818 ; *Pogg. Ann.*, **1**. 34, 1824 ; *Ann. Chim. Phys.*, (2), **17**. 7, 1821 ; O. Unverdorben, *Trommsdorff's Journ.*, **9**. 26, 1824 ; *Pogg. Ann.*, **7**. 311, 1826 ; A. von Kess and F. E. Lederer, *Rec. Trav. Chim. Pays-Bas.*, **46**. 453, 1927 ; E. Ludwig, *Liebig's Ann.*, **162**. 51, 1872 ; C. L. Reese, *Amer. Chem. Journ.*, **22**. 158, 1899 ; A. C. Robertson, *Journ. Amer. Chem. Soc.*, **48**. 2072, 1926 ; **49**. 1630, 1927 ; E. J. Guy and W. C. Bray, *ib.*, **46**. 1786, 1924 ; A. C. Chapman, *Analyst*, **29**. 346, 1904 ; M. Traube, *Ber.*, **22**. 1518, 1899 ; A. Bach, *ib.*, **35**. 872, 1902 ; E. H. Riesenfeld and A. Wesch, *ib.*, **41**. 2826, 1908 ; A. Wesch, *Ueber Chromsäurederivate*, Freiburg, 1908 ; J. Hargreaves and T. Robinson, *Brit. Pat. No.* 508, 1872 ; V. N. Ipatieff and B. A. Mourontseff, *Compt. Rend.*, **183**. 505, 1926 ; W. Ipatieff, *Ber.*, **59**. B, 1492, 1926 ; W. Ipatieff and A. Kisseleff, *ib.*, **59**. B, 1418, 1926 ; *Journ. Russ. Phys. Chem. Soc.*, **58**. 664, 686, 692, 698, 1926 ; E. Spitalsky, *Zeit. anorg. Chem.*, **56**. 72, 1907 ; E. Spitalsky and N. Koboseff, *Zeit. phys. Chem.*, **127**. 129, 1927 ; A. Mailfert, *Compt. Rend.*, **94**. 860, 1882 ; H. Moissan, *ib.*, **97**. 96, 1883 ; L. C. A. Barreswil, *ib.*, **16**. 1085, 1848 ; *Ann. Chim. Phys.*, (3), **20**. 364, 1848 ; H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, **1**. 352, 1851.

[2] H. Moissan, *Compt. Rend.*, **98**. 1581, 1884 ; *Bull. Soc. Chim.*, (2), **43**. 6, 1884 ; *Ann. Chim. Phys.*, (6), **5**. 468, 1885 ; E. Donath, *Zeit. anal. Chem.*, **18**. 78, 1879 ; M. M. Richter, *ib.*, **21**. 368,

1882; C. F. Mohr, *ib.*, **11.** 278, 1872; L. Henry, *Bull. Acad. Belg.*, (2), **21.** 230, 1866; N. A. Orloff, *Journ. Russ. Phys. Chem. Soc.*, **45.** 511, 1913; W. Autenrieth, *Ber.*, **35.** 2064, 1902; W. Manchot and R. Kraus, *ib.*, **39.** 3512, 1906; R. Kraus, *Untersuchungen über die Verbindungen von Chrom und Uran mit mehrwertigen Elementen*, Würzburg, 1906; L. L. de Koninck, *Bull. Assoc. Belg.*, **17.** 157, 1903; J. W. Thomas, *Journ. Chem. Soc.*, **33.** 367, 1878; A. Michael and A. Murphy, *Amer. Chem. Journ.*, **44.** 379, 1910; R. J. Meyer and H. Best, *Zeit. anorg. Chem.*, **22.** 192, 1899; P. A. Meerburg, *ib.*, **54.** 31, 1907; R. Luther and N. Schiloff, *Zeit. phys. Chem.*, **46.** 777, 1903; N. Schiloff, *ib.*, **27.** 513, 1898; R. Luther and T. F. Rutter, *Zeit. anorg. Chem.*, **56.** 1, 1907; N. R. Dhar, *ib.*, **121.** 151, 1922; C. Wagner and W. Preiss, *ib.*, **168.** 265, 1928; K. Seubert and J. Carstens, *ib.*, **50.** 53, 1906; M. Bobtelsky and A. Rosenberg, *ib.*, **177.** 137, 1928; **182.** 74, 1929; M. Bobtelsky and D. Kaplan, *ib.*, **177.** 119, 1928; M. Bobtelsky, *ib.*, **182.** 93, 1929; K. Seubert and A. Henke, *Zeit. angew. Chem.*, **13.** 1147, 1900; W. B. Morehouse, *Phys. Rev.*, (2), **27.** 794, 1926; R. H. Clark, *Journ. Phys. Chem.*, **11.** 353, 1907; R. E. de Lury, *ib.*, **7.** 239, 1903; J. M. Bell, *ib.*, **7.** 61, 1903; R. A. Gortner, *ib.*, **12.** 362, 1908; C. C. Benson, *ib.*, **7.** 1, 356, 1903; **8.** 116, 1904; S. S. Bhatnagar, R. N. Mathur and R. N. Kapur, *Phil. Mag.*, (7), **8.** 457, 1929; W. Preiss, *Ueber die Induktion der Reaktion zwischen Chromsäure und Iodide durch Ferrosalz*, München, 1927; W. Ostwald, *Zeit. phys. Chem.*, **2.** 137, 1888; A. Schükareff, *ib.*, **38.** 353, 1901; W. C. Bray, *ib*, **54.** 491, 1906; F. Penny, *Chem. Gaz.*, **10.** 392, 1852; *B.A. Rep.*, 37, 1852; M. H. Golblum and L. Lew, *Journ. Chim. Phys.*, **10.** 310, 1912; I. Walz, *Chem. News*, **26.** 245, 1872; K. H. Butler and D. McIntosh, *Trans. Roy. Soc. Canada*, (3), **21.** 19, 1927; R. F. Beard and N. W. Taylor, *Journ. Amer. Chem. Soc.*, **51.** 1973, 1929; M. Bobtelsky, *Zeit. anorg. Chem.*, **190.** 337, 1930; O. Ruff and H. Krug, *ib.*, **190.** 270, 1930; F. E. E. Germann and D. K. Shen, *Journ. Phys. Chem.*, **33.** 1583, 1929.

[3] H. Moissan, *Compt. Rend.*, **98.** 1581, 1884; *Bull. Soc. Chim.*, (2), **43.** 6, 1884; *Ann. Chim. Phys.*, (6), **5.** 468, 1885; J. B. Senderens, *Bull. Soc. Chim.*, (3), **6.** 802, 1891; A. W. Rakowsky and D. V. Tarassenkoff, *Journ. Russ. Phys. Chem. Soc.*, **60.** 7, 1928; K. Brückner, *Monatsh.*, **27.** 199, 1906; O. Harten, *Liebig's Ann.*, **37.** 350, 1841; M. Traube, *ib.*, **66.** 103, 1848; O. Brunck, *ib.*, **336.** 290, 1904; B. A. Bolley, *ib.*, **56.** 113, 1845; A. Schrötter, *ib.*, **48.** 225, 1843; P. Berthier, *Ann. Chim. Phys.*, (3), **7.** 78, 1843; H. Bassett, *Journ. Chem. Soc.*, **83.** 692, 1903; L. F. Gilbert, H. Buckley, and I. Merson, *ib.*, **121.** 1934, 1922; E. J. Bowen and C. W. Benson, *ib.*, 2353, 1919; R. Luther and T. F. Rutter, *Zeit. anorg. Chem.*, **54.** 16, 1907; A. W. Rakowsky and D. N. Tarassenkoff, *ib.*, **174.** 91, 1928; D. N. Tarassenkoff, *Arb. Russ. Inst. Pure Chem. Reagents*, 6, 1927; *Journ. Russ. Phys. Chem. Soc.*, **68.** 7, 1928; R. Kraus, *Untersuchungen über die Verbindungen von Chrom und Uran mit mehrwertigen Elementen*, Würzburg, 1906; W. Manchot and R. Kraus, *Ber.*, **39.** 3512, 1906; C. T. Kingzett, *Chem. News*, **40.** 96, 1879; **42.** 34, 242, 1880; **43.** 127, 1881; A. Longi, *Gazz. Chim. Ital.*, **26.** ii, 119, 1896; L. Longi and L. Bonavia, *ib.*, **26.** i, 327, 1896; F. J. Faktor, *Pharm. Post*, **34.** 485, 1901; C. Weltzien, *Liebig's Ann.*, **142.** 107, 1867; J. C. G. de Marignac, *Compt. Rend.*, **20.** 808, 1845; *Ann. Chim. Phys.*, (3), **14.** 252, 1845; L. I. de N. Ilosva, *Bull. Soc. Chim.*, (3), **2.** 734, 1889; A. Skrabal, *Zeit. Elektrochem.*, **14.** 529, 1908; A. Wesch, *Ueber Chromsäurederivate*, Freiburg, 12, 1908; E. H. Riesenfeld and A. Wesch, *Ber.*, **41.** 2826, 1908; H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, **1.** 352, 1851; G. Powarnin and M. Chitrin, *Journ. Russ. Phys. Chem. Soc.*, **41.** 1033, 1909; W. Diehl, *Zeit. anal. Chem.*, **19.** 306, 1880; J. Fritzsch, *Pogg. Ann.*, **50.** 540, 1840; *Journ. prakt. Chem.*, (1), **19.** 176, 1840; *Mém. Acad. St. Petersburg*, **6.** 181, 1839; H. B. Dunnicliff and C. L. Soni, *Journ. Phys. Chem.*, **33.** 81, 1929.

[4] S. S. Bhatnagar, R. N. Mathur and R. N. Kapur, *Phil. Mag.*, (7), **8.** 457, 1929; E. Schweizer, *Journ. prakt. Chem.*, (1), **39.** 269, 1846; J. Jacobson, *Liebig's Ann.*, **40.** 265, 1841; *Journ. prakt. Chem.*, (1), **23.** 467, 1841; H. Reinsch, *ib.*, (1), **28.** 391, 1843; T. Curtius and F. Schrader, *ib.*, (2), **50.** 320, 1894; P. Grouvelle, *Ann. Chim. Phys.*, (2), **17.** 349, 1821; C. W. Eliot and F. H. Storer, *Proc. Amer. Acad.*, **5.** 207, 1862; *Chem. News*, **6.** 121, 136, 145, 156, 169, 182, 207, 217, 1862; H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, **1.** 352, 1851; A. D. Mitchell, *Journ. Chem. Soc.*, **125.** 564, 1924; F. Wöhler, *Liebig's Ann.*, **34.** 236, 1840; H. Schiff, *ib.*, **106.** 116, 1858; O. Unverdorben, *Trommsdorff's Journ.*, **9.** 26, 1824; *Pogg. Ann.*, **7.** 311, 1826; R. Böttger, *Liebig's Ann.*, **57.** 134, 1846; S. A. Mumford and L. F. Gilbert, *Journ. Chem. Soc.*, **123.** 471, 1923; U. Roberts and F. Roncali, *L'Ind. Chimica*, **6.** 178, 1904; K. Seubert and J. Carstens, *Zeit. anorg. Chem.*, **56.** 357, 1908; F. Ephraim, *ib.*, **44.** 193, 1905; C. Reichard, *Ber.*, **30.** 1915, 1897; *Chem. Ztg.*, **24.** 563, 1900; R. E. de Lury, *Journ. Phys. Chem.*, **11.** 47, 1907; W. L. Miller, *ib.*, **11.** 17, 1907; R. Bunsen, *Liebig's Ann.*, **148.** 290, 1868; E. Zettnow, *Pogg. Ann.*, **143.** 468, 1871; G. Viard, *Compt. Rend.*, **124.** 148, 1897; M. Berthelot, *ib.*, **96.** 542, 1883; *Ann. Chim. Phys.*, (6), **1.** 92, 101, 1884; A. Oppenheim, *Bull. Soc. Chim.*, (2), **1.** 165, 1864; H. Moissan, *Compt. Rend.*, **98.** 1581, 1884; *Bull. Soc. Chim.*, (2), **43.** 6, 1884; *Ann. Chim. Phys.*, (6), **5.** 468, 1885; E. P. Wightman and S. E. Sheppard, *Phot. Journ.*, **68.** 201, 1928; E. Kopp, *Chem. News*, **9.** 278, 1864; A. Stiassny, *Dingler's Journ.*, **199.** 414, 1871; J. W. Slater, *Chem. Gaz.*, **11.** 329, 1853; P. Walden, *Zeit. anorg. Chem.*, **68.** 307, 1910; A. Rosenheim and F. Jacobsohn, *ib.*, **50.** 297, 1906; G. Wagner, *ib.*, **168.** 279, 1927; N. R. Dhar, *ib.*, **128.** 218, 1923; A. Skrabal, *Zeit. Elektrochem.*, **14.** 529, 1908; E. C. Franklin, *Amer. Chem. Journ.*, **20.** 827, 1898; E. J. Cuy and W. C. Bray, *Journ. Amer. Chem. Soc.*, **46.** 858, 1786, 1924.

[5] J. Hargreaves and T. Robinson, *Brit. Pat. No.* 506, 1872; H. Kunz-Krause and P. Manicke, *Ber. deut. pharm. Ges.*, **32.** 209, 1922; A. Gawalowsky, *Zeit. anal. Chem.*, **17.** 179, 1878; K. Someya, *Zeit. anorg. Chem.*, **159.** 158, 1927; C. Wagner, *ib.*, **168.** 279, 1928; M. Prud'homme,

§ 15. The Chromates. Monochromates

The normal chromates are to be regarded as salts of the dibasic **chromic acid,** or rather **metachromic acid,** H_2CrO_4; it is possible that the hypothetical **parachromic acid,** H_4CrO_5, is represented by some of the basic salts—$PbO.PbCrO_4$; and the hypothetical **orthochromic acid,** HCr_6O_6, represented by other basic salts—*e.g.* $2PbO.PbCrO_4$.

Bull. Soc. Mulhouse, **73**. 128, 1903 ; *Bull. Soc. Chim.*, (3), **29**. 306, 1903 ; A. Pictet, *Arch. Sciences Genève*, (4), **15**. 465, 1903 ; A. Pictet and P. Genequand, *Ber.*, **36**. 2218, 1903 ; H. E. Armstrong, *ib.*, **2**. 713, 1869 ; H. Wienhaus, *ib.*, **47**. 322, 1914 ; A. Naumann, *ib.*, **37**. 4328, 1904 ; **42**. 3790, 1909 ; **43**. 314, 1910 ; **47**. 1369, 1914 ; W. P. Jorissen and L. T. Reicher, *Zeit. Farben Textilchemie*, **2**. 431, 1903 ; A. N. Dey and N. R. Dhar, *Zeit. Elektrochem.*, **32**. 586, 1926 ; H. Vohl, *Liebig's Ann.*, **63**. 398, 1847 ; E. Ludwig, *ib.*, **162**. 47, 1872 ; A. Maus, *Pogg. Ann.*, **9**. 127, 1827 ; **11**. 83, 1827 ; J. M. Eder, *Monatsh.*, **6**. 503, 1885 ; R. C. Banerji and N. R. Dhar, *Zeit. anorg. Chem.*, **152**. 172, 1924 ; A. K. Bhattacharya and N. R. Dhar, *ib.*, **169**. 381, 1928 ; A. K. Bhattacharya and N. R. Dhar, *ib.*, **175**. 357, 1928 ; *Journ. Indian Chem. Soc.*, **6**. 173, 451, 1929 ; B. K. Mukerji, A. K. Bhattacharya and N. R. Dhar, *Journ. Phys. Chem.*, **32**. 1824, 1928 ; B. K. Mukerji and N. R. Dhar, *ib.*, **33**. 850, 1929 ; **7**. 677, 1930 ; N. R. Dhar, *Journ. Chem. Soc.*, **111**. 690, 707, 1917 ; **123**. 1856, 1923 ; L. F. Gilbert, *ib.*, **127**. 1541, 1925 ; E. J. Bowen and C. W. Bunn, *ib.*, 2353, 1927 ; M. A. Ilinsky and D. I. Kodner, *Journ. Russ. Phys. Chem. Soc.*, **60**. 193, 1928 ; B. V. Tronoff and A. A. Lukanim, *ib.*, **59**. 1157, 1927 ; B. V. Tronoff, V. F. Uradoff and M. I. Chizhova, *ib.*, **59**. 1149, 1927 ; M. Berthelot, *Compt. Rend.*, **70**. 256, 1870 ; E. Goldberg, *Zeit. wiss. Photochem.*, **4**. 95, 1906 ; R. Fittig, *Gött. Nachr.*, 25, 1862 ; R. Böttger, *Liebig's Ann.*, **57**. 134, 1846 ; *Materialien zur Versuche für chemischphysikalische Vorlesungen*, Frankfurt, 72, 1846 ; L. Cohn, *Arbeitsmethoden für organisch-chemische Laboratorien*, Leipzig, 671, 1923 ; K. Jablcznysky, *Zeit. anorg. Chem.*, **60**. 38, 1908 ; *Anz. Akad. Krakau*, 603, 1908 ; A. Schafarik, *Sitzber. Akad. Wien*, **47**. 254, 1863 ; *Journ. prakt. Chem.*, (1), **90**. 12, 1863 ; G. Ulrich and T. Schmidt, *Zeit. physiol. Chem.*, **55**. 25, 1908 ; A. Windaus, *ib.*, **100**. 167, 1917 ; R. Luther and G. S. Forbes, *Journ. Amer. Chem. Soc.*, **31**. 770, 1909 ; H. S. Fry, *ib.*, **33**. 698, 1911 ; R. M. Isham and C. E. Vail, *ib.*, **37**. 902, 1915 ; J. Jacobson, *Journ. prakt. Chem.*, (1), **33**. 467, 1841 ; *Liebig's Ann.*, **40**. 265, 1841 ; I. Guareschi, *Atti Accad. Torino*, **49**. 15, 1914 ; M. Michels, *Bull. Soc. Mulhouse*, **94**. 344, 1928 ; *Trans. Faraday Soc.*, **26**. 1, 1930 ; *Zeit. anorg. Chem.*, **176**. 372, 1928 ; D. S. Morton, *Journ. Phys. Chem.*, **33**. 1135, 1929 ; W. G. Vannoy, *ib.*, **33**. 1593, 1929 ; S. Takegami, *Bull. Japan. Chem. Soc.*, **4**. 156, 1929 ; E. Müller and P. Ekwall, *Zeit. Elektrochem.*, **35**. 84, 1929 ; E. Müller and J. Stscherbakow, *ib.*, **35**. 222, 1929 ; E. P. Wightman and S. E. Sheppard, *Phot. Journ.*, **68**. 201, 1928 ; E. B. Alekseevsky and A. P. Musakin, *Journ. Russ. Phys. Chem. Soc.*, **62**. 205, 1930 ; B. Neumann and C. Exssner, *Zeit. angew. Chem.*, **43**. 440, 1930.

[6] H. Moissan, *Compt. Rend.*, **98**. 1581, 1884 ; *Bull. Soc. Chim.*, (2), **43**. 6, 1884 ; *Ann. Chim. Phys.*, (6), **5**. 468, 1885 ; J. L. Gay Lussac and L. J. Thénard, *Recherches physicochimiques*, Paris, **1**. 517, 1811 ; L. F. Gilbert, *Journ. Chem. Soc.*, **127**. 1541, 1925 ; R. G. van Name and D. U. Hill, *Amer. Journ. Science*, (4), **42**. 301, 1916 ; (4), **45**. 54, 1918 ; J. Jacobson, *Journ. prakt. Chem.*, (1), **23**. 467, 1841 ; *Liebig's Ann.*, **40**. 265, 1841 ; P. Lebeau, *Bull. Soc. Chim.*, (3), **27**. 42, 1902 ; E. Heyn and O. Bauer, *Mitt. Materialprüf. Amt.*, **26**. 1, 1907 ; R. Bunsen, *Liebig's Ann.*, **38**. 257, 1866 ; L. Möser and W. Eidmann, *Ber.*, **35**. 535, 1902 ; W. Manchot and R. Kraus, *ib.*, **39**. 3512, 1905 ; R. Kraus, *Untersuchungen über die Verbindungen von Chrom und Uran mit mehrwertigen Elementen*, Würzburg, 1906 ; K. Someya, *Zeit. anorg. Chem.*, **152**. 368, 386, 1926.

[7] A. Scheurer-Kestner, *Compt. Rend.*, **50**. 50, 1860 ; A. Charriou, *Journ. Chim. Phys.*, **23**. 621, 1926 ; J. F. John, *Schweigger's Journ.*, **3**. 378, 1811 ; *Gehlen's Journ.*, **3**. 452, 1804 ; **4**. 436, 1804 ; F. Fischer, *Zeit. Elektrochem.*, **10**. 430, 1904 ; E. Murmann, *Oester. Chem. Ztg.*, **1**. 383, 1898 ; R. Lang, *Zeit. anorg. Chem.*, **170**. 387, 1928 ; R. J. Lang and F. Kurtz, *ib.*, **181**. 111, 1929 ; R. Lang and J. Zwerina, *ib.*, **170**. 389, 1928 ; J. Zwerina, *Ueber einige Arsenitmethoden, insbesondere unter Anwendung der Manganosalz- und Jodkatalyse*, Brünn, 1927 ; A. Schükareff, *Zeit. phys. Chem.*, **38**. 353, 1901 ; E. Müller and H. Kogert, *ib.*, **136**. 437, 1928 ; A. Geuther, *Liebig's Ann.*, **106**. 239, 1858 ; H. Schwarz, *ib.*, **69**. 209, 1849 ; W. Manchot, *ib.*, **325**. 105, 1902 ; *Ber.*, **39**. 488, 352, 1906 ; C. Rube, *Journ. prakt. Chem.*, (1), **95**. 53, 1865 ; N. R. Dhar, *Journ. Chem. Soc.*, **111**. 690, 707, 1917 ; V. H. Veley, *ib.*, **55**. 361, 1889 ; C. C. Benson, *Journ. Phys. Chem.*, **7**. 1, 356, 1903 ; **8**. 116, 1904 ; W. L. Miller, *ib.*, **11**. 15, 1907 ; R. A. Gortner, *ib.*, **12**. 632, 1908 ; N. Schiloff, *Zeit. phys. Chem.*, **42**. 641, 1903 ; R. Luther and N. Schiloff, *ib.*, **46**. 777, 1903 ; M. Neidle and J. C. Witt, *Journ. Amer. Chem. Soc.*, **37**. 2360, 1915 ; **38**. 47, 1916 ; R. G. van Name and F. Fenwick, *ib.*, **47**. 19, 1925 ; R. Luther and T. F. Rutter, *Zeit. anorg. Chem.*, **54**. 1, 1907 ; S. Orlowsky, *ib.*, **170**. 184, 1928 ; J. Schabus, *Sitzber. Akad. Wien*, **6**. 396, 1851 ; F. Penny, *Chem. Gaz.* **8**. 330, 1850 ; *Journ. Chem. Soc.*, **4**. 239, 1851 ; K. Someya, *Zeit. anorg. Chem.*, **152**. 360, 386, 1926 ; R. G. van Name and D. U. Hill, *Amer. Journ. Science*, (4), **42**. 301, 1916 ; (4), **45**. 54, 1918 ; H. Moissan, *Compt. Rend.*, **98**. 1581, 1884 ; *Bull. Soc. Chim.*, (2), **43**. 6, 1884 ; *Ann. Chim. Phys.*, (6), **5**. 468, 1885 ; E. Heyn and O. Bauer, *Mitt. Materialprüf. Amt.*, **26**. 1, 1907 ; J. Jacobson, *Journ. prakt. Chem.*, (1), **23**. 467, 1841 ; *Liebig's Ann.*, **40**. 265, 1841.

L. N. Vauquelin,[1] J. B. Richter, and H. Moser obtained what was regarded as **ammonium chromate,** $(NH_4)_2CrO_4$, by evaporating an aq. soln. of chromic acid mixed with an excess of ammonia. J. J. Pohl said that with the ammonia in large excess, yellow crystals of *ammonium oxychromate,* $(NH_4)_2O.4(NH_4)_2CrO_4$, are formed; which, according to J. Schabus, are monoclinic prisms with the axial ratio $a : b : c = 0·7458 : 1 : 0·4955$, and $\beta = 106° 15'$. C. F. Rammelsberg doubted whether this compound really exists; J. J. Pohl's analysis was imperfect—only the chromium was determined. E. Jäger and G. Krüss showed that when an aq. soln. of chromic acid is evaporated with ammonia, the salt is partially decomposed with evolution of ammonia, and a mixture of chromate and dichromate is always obtained; even when the soln. is evaporated at 50° to 60°, reddish-yellow crystals containing 59·19 per cent. of chromic oxide are obtained, and at ordinary temp., also, a mixture of the two salts is produced. According to Y. T. Gerasimoff, the salt cannot be conveniently prepared by double decomposition, but it can be made by neutralizing chromic acid with ammonia. Ammonium chromate can be prepared by treating chromic acid, free from sulphuric acid, with aq. ammonia of sp. gr. 0·9, adding ammonia and warming gently until the solid salt which separates is redissolved, and then placing the soln. in a freezing mixture. It crystallizes in long, golden needles. E. Maumené said that a conc. soln. of chromic acid or potassium dichromate neutralized by ammonia, deposits ammonium chromate in yellow, crystalline tufts, which resemble those of the potassium salt, but soon lose ammonia, and change into the dichromate. The salt is best crystallized by evaporating the slightly ammoniacal soln. over quicklime, and should be kept in sealed vessels. H. Hirzel obtained ammonium chromate by gradually adding chromyl chloride to an excess of aq. ammonia, and evaporating the soln. below 60°. The first crop of crystals is ammonium chromate; and the next crop, ammonium chloride. The salt was purified by recrystallization. Analyses by E. Kopp, S. Darby, and E. Jäger and G. Krüss agreed with the formula $(NH_4)_2CrO_4$. E. Maumené, L. N. Vauquelin, H. Moser, and E. Jäger and G. Krüss showed that when the aq. soln. of the salt is repeatedly evaporated, it is first converted into the dichromate, and then into a brown oxide. E. Jäger and G. Krüss could not prepare any basic salt like that reported by J. J. Pohl; nor did F. A. H. Schreinemakers observe the formation of any basic salt during his study of the ternary system: CrO_3–NH_3–H_2O, at 30°. The following is a selection from the solubility data for sat. soln.—concentrations are expressed in percentages:

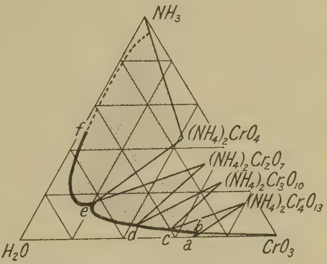


FIG. 29.—Equilibrium Diagram for the Ternary System: CrO_3–NH_3–H_2O at 30°.

CrO_3 . .	6·933	9·966	14·486	18·98	27·09	25·43	42·437
NH_3 . .	22·348	16·529	10·780	6·49	6·87	4·34	3·1483
Solids	$(NH_4)_2CrO_4$				$(NH_4)_2Cr_2O_7$		
CrO_3 . .	44·08	52·41	56·62	58·87	63·60	62·94	62·28
NH_3 . .	2·271	1·107	0·9496	0·6485	0·3991	0·2094	—
Solids	$(NH_4)_2Cr_3O_{10}$			$(NH_4)_2Cr_4O_{13}$		CrO_3	

The results are shown respectively in Fig. 29. The region above the line *abcdef* refers to unsaturated soln.; *ab* represents soln. in equilibrium with solid chromium trioxide; *bc*, with solid ammonium tetrachromate; *cd*, with solid trichromate; *de*, with solid dichromate; and *ef*, with solid monochromate. Ammonia was here selected as one of the components because $(NH_4)_2O$ is not stable.

According to E. Jäger and G. Krüss, the golden-yellow needles are monoclinic prisms with the axial ratios $a : b : c = 1·9603 : 1 : 2·4452$, and $\beta = 64° \ 47'$. E. Herlinger studied the structure of the crystals. J. W. Retgers said that ammonium chromate is not isomorphous with the potassium chromate family. The other measurements of G. N. Wyrouboff made it appear as if the salt is dimorphous, like potassium chromate ; but more data are required to confirm these results ; however, he found that ammonium chromate forms an isomorphous series of solid soln. with anhydrous, rhombic sodium sulphate, and another series with anhydrous, monoclinic sodium sulphate. There is a gap between the two series, and hence, the salt exhibits what has been called a labile dimorphism. T. Ishikawa studied the system : $(NH_4)_2CrO_4$–$(NH_4)_2SO_4$–K_2SO_4–K_2CrO_4. S. Araki found that the solubility curve in the system : $(NH_4)_2CrO_4$–$(NH_4)_2SO_4$–H_2O at 25° has two branches with two series of solid soln. No solid soln. occur with ammonium sulphate between 2·90 and 21·50 molar per cent.—*BC*, Fig. 30. He also studied the system : $(NH_4)_2CrO_4$–K_2CrO_4–H_2O. H. G. C. Schröder gave 1·866 for the sp. gr. of ammonium monochromate ; F. W. Clarke, 1·917 at 12° ; and E. Jäger and G. Krüss, 1·886, at 11°. K. F. Slotte found the sp. gr. of aq. soln. with 10·52, 19·75, and 28·04 per cent. of $(NH_4)_2CrO_4$ to be respectively 1·0633 at 13°, 1·1197 at 13·7°, and 1·1727 at 19·6° ; and the viscosity (water 100) respectively 108·3, 120·3, and 137·9 at 10° ; 85·2, 95·5, and 110·1 at 20° ; and 57·8, 66·1, and 76·9 at 40°. The sp. ht. of aq. soln. of a mol of ammonium chromate with *n* mols of water was found by J. C. G. de Marignac to be 0·7967 for $n=25$; 0·8767 for $n=50$; 0·9304 for $n=100$; and 0·9630 for $n=200$. The subject was discussed by N. de Kolossowsky. F. Morges gave for the heat of neutralization : $(H_2CrO_{4aq.}, 2NH_4OH_{aq.}) = 22·2$ Cals. at 12° ; and M. Berthelot, 24·42 Cals. at 19·5°. F. Morges also gave $(NH_4)_2Cr_2O_{7aq.}, 2NH_4OH_{aq.}) = 20·4$ Cals. at 12°. P. Sabatier found —5·8 Cals. for the heat of soln. of a mol of ammonium chromate in 200 parts of water at 18°. The spectroscopic observations of D. Brewster, and J. H. Gladstone have been previously discussed. M. G. Mellon studied the colour of soln. of different concentration. I. Plotnikoff and M. Karshulin measured the absorption spectrum and the region of photochemical sensitivity for collodion films with methyl alcohol as acceptor. M. S. Sherrill found the eq. conductivity, λ mho, corrected for hydrolysis, for *m* grm.-equivalents of the salt per litre at 18°, to be .

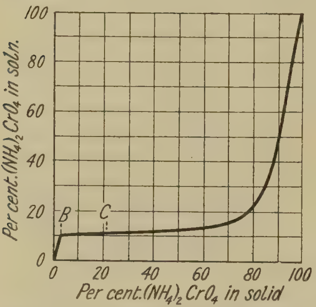


FIG. 30.—Solubility of Binary Mixtures : $(NH_4)_2CrO_4$–$(NH_4)_2SO_4$ at 25°.

m . .	0·005	0·01	0·02	0·04
λ . .	123·4	118·4	112·5	105·5

and C. Watkins and H. C. Jones gave for the molar conductivity, μ mho, of a mol of salt in *v* litres,

v	. .	4	8	16	32	128	512	1024
μ	0° .	99·8	109·3	117·8	126·9	144·0	154·1	152·4
	15° .	146·0	159·7	173·9	187·9	214	227	227
	25° .	—	193·9	213	230	263	280	279
	35° .	—	230	282	274	312	333	333

The calculated percentage ionizations at 0° and 35° are :

v . . .	4	8	16	32	128	512
0° . .	66·7	70·8	76·4	82·3	93·4	100·0
35° . .	—	68·8	75·7	82·2	93·6	100·0

M. S. Sherrill calculated the hydrolysis of a 0·05 molar soln. at 18° to be 2·7 per cent. According to A. Naumann and O. Rücker, a not very exact distillation process showed that the hydrolysis expressed in percentages of the ammonia content, for soln. containing *m* gram-equivalents of salt per litre, was:

m	1·0	0·4	0·1	0·025	0·0025
Hydrolysis	31·0	32·6	36·8	42·0	49·0

E. Jäger and G. Krüss said that ammonium chromate is not particularly stable in the dry state, and on exposure to air, it gradually turns reddish-yellow owing to the formation of the dichromate; it also decomposes in a dry atm., or when gently heated. A. Maus observed that decomposition occurs with glowing, when heated, and the green chromic oxide which remains is readily soluble in acids. W. C. Ball observed that when heated, it decomposes like the dichromate (*q.v.*). According to E. Maumené, ammonium chromate yields a brown oxide, CrO_2, when heated at 204°, identical with the oxide which was described by L. N. Vauquelin as precipitated on heating the aq. soln., although in all probability it is formed only on the superheated sides of the vessel. When the temp. is raised to 220° or 225°, explosive decomposition occurs, and the oxide CrO is formed, which, however, takes fire at once, and burns to the green oxide Cr_2O_3; it is probable that the compound $N_2H_4CrO_3$ is formed as an intermediate product. F. A. H. Schreinemakers found that 40·46 grms. of the salt dissolve in 100 grms. of water at 30°—*vide supra.* In consequence of hydrolysis, the soln., as noticed by L. N. Vauquelin, H. Moser, and E. Jäger and G. Krüss, reacts alkaline, and gradually loses ammonia. Consequently, as pointed out by E. Maumené, it should be crystallized from aq. soln. in an atm. of ammonia. M. Gröger observed that the aq. soln. containing the molar proportions $2NH_3 : CrO_3$ is orange coloured, not yellow. He therefore assumed that the soln. contains a large proportion of dichromate: $2(NH_4)_2CrO_4 \rightleftharpoons 2NH_3+H_2O+(NH_4)_2Cr_2O_7$. C. Paal and G. Brünjes found that in the presence of colloidal palladium, a soln. of ammonium chromate is reduced by hydrogen. W. Müller found that the vapour of carbon disulphide converts it into chromium sulphide and oxide. H. Stamm measured the solubility of the salt in aq. ammonia and found that soln. with 0, 1·818, and 3·436 mols of NH_3 per 100 grms. of water dissolve, respectively, 0·200, 0·066, and 0·043 mol of $(NH_4)_2CrO_4$. E. C. Franklin found that the salt is sparingly soluble in liquid ammonia; and A. Naumann, sparingly soluble in acetone.

G. C. Gmelin,[2] C. F. Rammelsberg, and L. Schulerud prepared **lithium chromate,** $Li_2CrO_4.2H_2O$, by evaporating an aq. soln. of lithium carbonate in chromic acid. J. W. Retgers said that if the soln. be evaporated at this temp., or if the salt be heated to 150°, the anhydrous salt is formed, and it consists of needle-like crystals probably isomorphous with anhydrous lithium sulphate. F. Mylius and R. Funk said that a soln. of the salt sat. at 18° contains 52·6 grms. of Li_2CrO_4 per 100 grms. of water; W. Kohlrausch said that 100 c.c. of soln. at 18° contain 85 grms. Li_2CrO_4; P. P. von Weimarn, 100 grms. of water at 20° dissolve 111 grms. of salt, and F. A. H. Schreinemakers said 99·94 grms. at 30°. The salt deposited from its aq. soln. is the *dihydrate*, $Li_2CrO_4.2H_2O$, as proved by the analyses of C. F. Rammelsberg, and L. Schulerud. F. A. H. Schreinemakers observed that the ternary system: $Li_2O–CrO_3–H_2O$, at 30°, contains the following percentage proportions of lithium oxide and chromium trioxide:

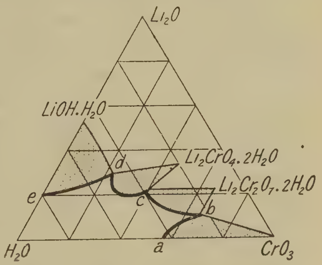


FIG. 31.—Equilibrium Diagram for the Ternary System: $Li_2O–CrO_3–H_2O$ at 30°.

CrO_3	—	22·51	37·50	38·55	43·40	49·60	67·73	63·26	62·28
Li_2O	7·09	9·88	16·34	11·44	11·81	7·33	5·69	2·14	—
Solids		$LiOH.H_2O$		$Li_2CrO_4.2H_2O$		$Li_2Cr_2O_7.2H_2O$		CrO_3	

The results are summarized in Fig. 31; the curve *ab* refers to soln. in equilibrium with solid chromium trioxide; *bc*, with solid $Li_2Cr_2O_7.2H_2O$; *cd*, with solid $Li_2CrO_4.2H_2O$; and *de*, with solid $LiOH.H_2O$. G. C. Gmelin said that lithium chromate furnishes orange-yellow, rhombic prisms, or dendritic masses, which, according to C. F. Rammelsberg, have the axial ratios $a:b:c=0·662:1:0·466$. F. Mylius and J. von Wrochem found that the soln. sat. at 18°, has a sp. gr. 1·574; A. Heydweiller gave for the sp. gr. of gram-equivalent soln. at 18°/18°,

	0·0815N-	0·1629N-	0·4115N-	0·823N-	2·057N-	4·115N-
Sp. gr. . .	1·00458	1·00902	1·02052	1·04437	1·10746	1·20659

C. F. Rammelsberg said that the salt is deliquescent, but when confined over conc. sulphuric acid, it effloresces; and, added L. Schulerud, it loses its water of crystallization at 130°, and melts at a higher temp. P. P. von Weimarn added that when the molten mass is rapidly cooled, it furnishes a transparent glass. G. Tammann found that 4·63, 20·23, 41·93, and 59·09 grms. of lithium chromate in 100 grms. of water lower the vap. press. respectively 11·5, 53·6, 131·2, and 205·2 mm. A. Heydweiller found the indices of refraction of 0·1, 0·5, 1·0, and 4·0N-Li_2CrO_4 are respectively 1·33529, 1·34307, 1·35251, and 1·40612 for the *D*-line at 18°; and the eq. electrical conductivities, λ mhos, of 0·0815, 0·4115, and 4·115N-soln. are respectively $\lambda=76·02$, 59·67, and 22·73 at 18°. C. Watkins and H. C. Jones gave for molar conductivity, μ mhos, for a mol of salt in v litres of water,

v	. . .	8	16	32	128	512	1024	2048
μ	0° . .	80	88	96	108	113	115	122
	15° . .	120	132	146	165	175	177	179
	25° . .	149	164	181	206	129	220	223
	35° . .	180	200	219	252	265	267	268

The percentage ionizations at 0° and 35° are:

v . .	8	16	32	128	512	1024	2048
0° . .	65·4	72·4	78·7	89·0	93·2	94·7	100·0
35° . .	67·2	74·5	81·7	94·0	99·0	99·5	100·0

H. Traube said that complex **lithium potassium sulphatochromate,** $Li_2CrO_4.K_2SO_4$, furnishes hexagonal crystals. C. F. Rammelsberg prepared what he regarded as **ammonium lithium chromate,** $(NH_4)LiCrO_4.2H_2O$, in non-deliquescent crystals from a soln. of the component salts.

Methods indicated in connection with the extraction of chromium from chromite can be made to yield **sodium chromate,** Na_2CrO_4. H. Moser[3] obtained it by fusing chromite with sodium hydroxide and nitrate, and crystallizing from an aq. soln. of the cold cake; and H. Kopp, by fusing chromic oxide with sodium nitrate, etc. J. d'Ans and J. Löffler obtained the chromate amongst the products of the action of chromic oxide on sodium hydroxide. M. R. Nayer and co-workers found that sodium carbonate and chromic oxide readily interact to form chromate at temp. below 660°; the salt melts at 800° and remains undecomposed after prolonged heating at 1000°. Ferric oxide and, to a greater extent, calcium oxide, accelerate the formation of chromate in mixtures of sodium carbonate and chromic oxide by preventing the mass from fusing and thus allowing better access of air. H. Moser obtained sodium chromate by neutralizing a soln. of chromic acid with sodium carbonate; and S. W. Johnson, by saturating a soln. of potassium dichromate with sodium carbonate and crystallizing the liquid. The salt can be so obtained free from potassium salts. M. de K. Thompson and co-workers, and A. J. B. Jouve and A. Helbronner obtained sodium chromate by electrolyzing sodium hydroxide soln. with ferrochromium anodes. If the aq. soln. be evaporated above 30°, H. Kopp, and J. W. Retgers said that the anhydrous salt is obtained; H. Traube gave 60° to 70°. Actually, the transition temp. is near 68°, Fig. 33. T. W. Richards and G. L. Kelley gave 62·8°. H. Traube added that the *dihydrate*, $Na_2CrO_4.2H_2O$, reported by G. N. Wyrouboff, is the imperfectly-dried, anhydrous salt.

J. W. Retgers said that the anhydrous sodium chromate forms yellow, columnar crystals, probably rhombic, and not isomorphous with sodium sulphate; H. Traube said that the two salts are isomorphous; and gave for the rhombic, bipyramidal crystals the axial ratios $a : b : c = 0·4643 : 1 : 0·7991$. The (010)-cleavage is perfect. J. Traube and W. von Behren studied the crystallization of the salt. E. Flach showed that sodium chromate and sulphate are completely miscible and isomorphous. The effect of the sulphate on the transition points of the chromate is illustrated by Fig. 32. C. Leenhardt studied the speed of crystallization of the hydrates.

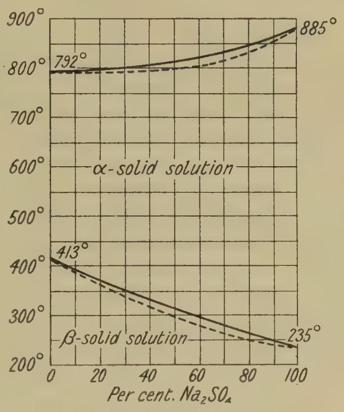


FIG. 32.—Effect of Sodium Sulphate on the Freezing and Transition Points of Sodium Chromate.

The existence of three hydrates has been established. F. W. Clarke gave 2·710 to 2·736 for the sp. gr.; and I. Traube added that the drop weight of the salt, at its m.p., is 328·2. The *tetrahydrate*, $Na_2CrO_4.4H_2O$, was prepared by D. Gernez by evaporating a supersaturated soln. of the decahydrate, or by contact of the soln. with the anhydrous salt. H. Traube obtained it from a conc soln. at 50°; and G. N. Wyrouboff, at 25° to 29°. J. Zehenter neutralized a soln. of potassium dichromate with sodium carbonate, and crystallized the mother-liquor after the separation of the $3K_2CrO_4.Na_2CrO_4$. The sulphur-yellow, acicular crystals were found by H. Traube to be monoclinic prisms with the axial ratios $a : b : c = 1·1112 : 1 : 1·0624$. E. Herlinger studied the structure of the crystals. T. W. Richards and W. B. Meldrum observed the formation of isomorphous mixtures of $Na_2SO_4.4H_2O$ and $Na_2CrO_4.4H_2O$. L. Delhaye measured the optical properties of the monoclinic crystals of the tetrahydrate prepared by allowing a soln. of sodium chromate, sat. at 50°, to cool to about 27°, filtering, and keeping for several days with occasional shaking. He gave for the optic axial angle $2V = 30° 50'$ for $\lambda = 462\mu\mu$; $29° 52'$ for $\lambda = 502\mu\mu$; $25° 33'$ for $\lambda = 536\mu\mu$; $21° 49'$ for $\lambda = 563\mu\mu$; and $16° 56'$ for $\lambda = 582\mu\mu$; and for the indices of refraction,

λ	535	573	589	600	625	650	670$\mu\mu$
α	1·576	1·566	1·561	1·559	1·551	1·545	1·536
β	1·471	1·457	1·447	1·440	1·383	1·291	1·285
γ	1·342	1·328	1·321	1·317	1·308	1·297	1·221

G. N. Wyrouboff gave for the optic axial angle $2E = 16° 10'$ for red-light, and 36° 22′ for green-light; he also said that the salt is somewhat deliquescent, and loses 2 mols. of water at 110°, and the rest at 250°; while H. Traube said that the salt loses water if allowed to stand in air for some time, and all the water is expelled at 150°. F. Mylius and R. Funk gave for the percentage solubility of the tetrahydrate—stable between 25·9° and 68°, Fig. 33—

	25·6°	36·0°	45·0°	54·5°	65·0°
S	46·08	47·98	50·20	52·28	55·23

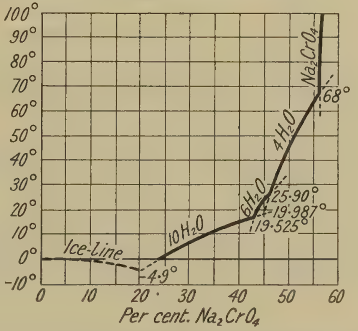


FIG. 33.—Solubility Curve of Sodium Chromate.

H. Salkowsky obtained the *hexahydrate*, $Na_2CrO_4.6H_2O$, accidentally from the mother-liquors of a soln. out of which the salt, $Na_2CrO_4.4H_2O$, had been crystallized. It crystallized in triclinic plates, and further crops were obtained by seeding sat. soln. of sodium chromate with it.

The percentage solubility of the hexahydrate—stable between 19·526° and 25·90°, Fig. 33—is:

	17·7°	19·2°	21·2°	24·7°	26·6°
S . . .	43·65	44·12	44·64	45·75	46·28

The *decahydrate*, $Na_2CrO_4.10H_2O$, is the salt obtained when the soln. is crystallized at ordinary temp., and it is the form stable below 19·526°. The crystals obtained by H. Moser, and J. F. John were lemon-yellow, and had a rough, metallic taste, and alkaline reaction. H. J. Brooke found that the monoclinic crystals, isomorphous with decahydrated sodium sulphate, have the axial ratios $a:b:c$ $=1·1127:1:1·2133$, and $\beta=107°\ 43'$; V. Rosiczky gave 1·1038 : 1 : 1·2351, and $\beta=72°\ 28°$. I. Takeuchi thought that a definite sodium trisulphatochromate, $2Na_2SO_4.Na_2CrO_4.30H_2O$, was formed at 25°, but Y. Osaka and R. Yoshida found that it is not a definite compound. Rather is it a solid soln. No solid soln. exists at 33°. At 28° and 31°, the chromate exists as the tetrahydrate and its solubility in the sulphate as the decahydrate decreases as the temp. rises, the molar fraction being 0·16 at 28° and 0·04 at 31°. G. N. Wyrouboff gave for the optical axial angle of the decahydrated chromate $2Y=83°\ 56'$ for red-light, and 82° 20′ for green-light. F. W. Clarke gave 1·483 for the sp. gr., and V. Rosiczky, 1·526. H. Kopp said that the crystals melt by the heat of the hand; S. W. Johnson gave 20°–21° for the m.p.; W. A. Tilden, and M. Berthelot gave 23°; J. L. R. Morgan and H. K. Benson, 19·92°; and F. Mylius and R. Funk said that there is a congruent m.p. at 21°. The m.p. lies in the region of instability of the hydrate since at 19·525°, there is a transformation into the hexahydrate with partial melting. T. W. Richards and G. L. Kelley suggested this incongruent m.p. as a fixed point in thermometry. G. Tammann found that the transition temp., θ, for $Na_2CrO_4.10H_2O \rightleftharpoons Na_2CrO_4.6H_2O + 4H_2O$, is lowered by an increase of press. p kgrms. per sq. cm., so that:

p . . .	1		400		600		1000		2300		3050
θ . . .	19·60°		18·50°		17·50°		14·90°		7·00°		0·00°
dp/θ . .		350		200		150		165		110	

This agrees with R. Hollmann's observations that the decahydrate contracts on fusion 0·010 c.c. per gram of salt. H. J. Brooke, and T. Thomson said that the crystals effloresce very rapidly in cold, dry air; and, added H. Moser, they become moist only in a damp. atm. H. Lescoeur found that the vap. press. of the sat. soln. is 10·6 mm. at 20° so that if the partial press. of the water-vapour in atm. air exceeds this, the salt will be deliquescent. F. Mylius and R. Funk found the percentage solubility of the decahydrate—stable below 19·256°—is:

	0°	10·0°	18·5°	19·5°	21·0°
S . . .	24·04	33·41	41·65	44·78	47·40

Observations on the solubility were made by F. Kohlrausch, F. Mylius and R. Funk, I. Takeuchi, and H. Salowsky. T. W. Richards and co-workers gave for the transition point between the decahydrate and the hexahydrate 19·525° to 19·63° with 44·2 per cent. Na_2CrO_4; T. W. Richards and R. C. Wells, 26·6°; T. W. Richards and G. L. Kelley gave 25·90° and H. Salkowsky 26·6° with 46·3 per cent. Na_2CrO_4 for the transition point between the hexahydrate and the tetrahydrate; and F. Mylius and R. Funk, about 68° with 55·2 per cent. Na_2CrO_4 for the transition temp. between the tetrahydrate and the anhydrous salt. J. Zeltner gave −4·9 for the eutectic temp. between ice and the decahydrate. The percentage solubilities can be summarized:

	0°	10°	19·525°	21·2°	25·90°	40°	68°	80°	100°
S . . .	24·1	33·4	44·2	44·6	46·3	49·0	55·2	55·3	55·8
	$Na_2CrO_4.10H_2O$			$Na_2CrO_4.6H_2O$		$Na_2CrO_4.4H_2O$		Na_2CrO_4	

The results are plotted in Fig. 34. There is a metastable region; F. Mylius and R. Funk gave for the solubility in this region 47·4 per cent. Na_2CrO_4 at 21° with the decahydrate as solid phase ; and the transition point 19·987° for the decahydrate and tetrahydrate. E. W. Washburn and E. R. Smith gave 19·51 for the transition temp. F. A. H. Schreinemakers observed that in the ternary system : Na_2O–$CrO_3.H_2O$ at 30°, when concentrations are expressed in percentages,

CrO_3 .	0	2·0	10·21	10·22	10·74	19·26	28·82	48·70
Na_2O .	42·0	41·44	29·70	29·39	25·55	22·98	17·88	16·49
Solids	$NaOH.H_2O$		Na_2CrO_4		$Na_4CrO_5.13H_2O$		$Na_2CrO_4.4H_2O$	

CrO_3 .	48·70	55·09	66·13	67·37	68·46	66·88	65·72	64·43
Na_2O .	16·49	14·44	13·70	12·50	10·95	9·85	6·31	4·51
Solids		$Na_2Cr_2O_7.2H_2O$		$Na_2Cr_3O_{10}.H_2O$	$Na_2Cr_4O_{15}.4H_2O$		CrO_3	

The solubility curve *ab* refers to the solid phase chromic acid; *bc*, to $Na_2Cr_4O_{13}.4H_2O$; *cd*, to $Na_2Cr_3O_{10}.H_2O$; *de*, to $Na_2Cr_2O_7.2H_2O$; *ef*, to $Na_2CrO_4.4H_2O$; *fg*, to $Na_4CrO_5.13H_2O$; *gh*, to Na_2CrO_4 ; and *hi*, to $NaOH.H_2O$. The basic salt, **sodium oxychromate,** $Na_4CrO_5.13H_2O$, or $Na_2O.Na_2CrO_4.13H_2O$, was obtained by F. Mylius and R. Funk from an aq. soln. of chromium trioxide sat. with sodium hydroxide. The pale-yellow crystals melt at 50° with the separation of sodium chromate. The aq. soln. saturated at 18° contains 37·5 per cent. of the anhydrous salt, and has a sp. gr. 1·446 ; and in soln. the salt is probably hydrolyzed. F. A. H. Schreinemakers said that it dissolves undecomposed in water, and the aq. soln. at 30° has 41·3 per cent. of the salt. F. Mylius and R. Funk gave for the percentage solubility :

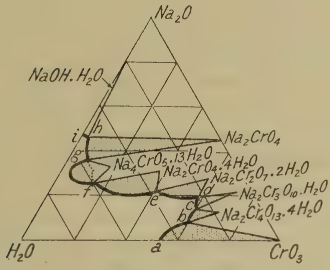


FIG. 34.—Equilibrium Diagram for the Ternary System : Na_2O–CrO_3–H_2O at 30°.

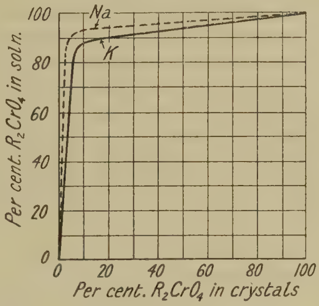


FIG. 35. — Crystallization of Mixed Solutions of Alkali Chromates and Sulphates.

	0°	10°	20·5°	27·7°	35°	37°
S . .	33·87	35·58	38·05	40·09	44·09	45·13

E. Flach studied the equilibrium between mixed soln. of sodium chromate and sulphate at 70° and the results are summarized in Fig. 35. With soln. containing 22, 62, 82, 91·5, and 96·5 per cent. of Na_2CrO_4, the separated crystals had, respectively, 0·21, 1·79, 3·45, 10·99, and 62·91 per cent. Na_2CrO_4 ; 99·16, 96·14, 94·58, 84·43, and 31·50 per cent. Na_2SO_4 ; and 0·63, 2·07, 1·99, 4·58, and 5·59 per cent. of water.

F. Mylius and R. Funk gave 1·409 for the sp. gr. of a soln. sat. at 18° ; A. Heydweiller, for soln. with 0·0533, 0·1066, 1·066, and 2·132 mols Na_2CrO_4 per litre at 18°, respectively 1·0077, 1·0152, 1·1442, and 1·2758 ; and H. C. Jones and H. P. Bassett, for soln. at 18°,

Na_2CrO_4 .	0·81	1·60	3·15	6·14	8·98	11·69	14·28 per cent.
Sp. gr. .	1·0075	1·0152	1·0287	1·0561	1·0834	1·1100	1·1366 ,,

K. F. Slotte found the sp. gr. of aq. soln. containing 5·76, 10·62, and 14·81 per cent. sodium chromate to be respectively 1·0576 at 17·4°/4°, 1·1125 at 17·1°/4°, and

1·1604 at 20·7°/4° ; and the viscosities (water 100), respectively at 10°, 117, 140·9, and 174 ; at 20°, 90·8, 108·3, and 132·5 ; at 30°, 72·8, 86·6, and 105·5 ; and at 40°, 59·8, 71·3, 85·9. J. L. R. Morgan and E. Schramm gave for the surface tension θ dynes per cm. :

Na_2CrO_4 .	4·45	12·67	24·05	34·91	45·25	49·81	53·13 per cent.
θ . .	71·64	73·35	76·48	81·52	89·73	95·36	97·46 ,,

For the observations of L. J. Simon on the viscosity of the soln. *vide infra*, potassium chromate. J. J. Coleman found that normal soln. of sodium molybdate, chromate, and tungstate diffused so that respectively 28, 25, and 17 per cent. rose 75 mm. in 30 days at 12·5°. J. C. G. de Marignac found for the sp. ht. between 21° and 52°, for soln. with 25, 50, 100, and 200 mols of water per mol of Na_2CrO_4, respectively 0·7810, 0·8560, 0·9134, and 0·9511. The subject was discussed by N. de Kolossowsky. G. Tamman observed the lowering of the vap. press. for soln. with 7·50, 30·88, 47·19, and 72·43 grms. of Na_2CrO_4 per 100 grms. of water, respectively 13·3, 61·6, 102·2, and 159·3 mm. of mercury—*vide supra*, for H. Lescoeur's observation. H. C. Jones and H. P. Bassett found the lowering of the f.p. for soln. with 0·1, 0·3, 0·6, and 1·0 mols of Na_2CrO_4 per litre to be respectively 0·450°, 1·230°, 2·345°, and 3·800°. F. Morges gave for the heat of neutralization of aq. soln. $(H_2CrO_4,2NaOH)$ =23·67 Cals. at 18° ; J. Thomsen, $(H_2CrO_4(400\text{ aq.}),2NaOH(400\text{ aq.}))$=24·72 Cals., or, according to M. Berthelot, 28·72—30(θ—18) Cals. at θ° ; and $2H_2CrO_4(800\text{ aq.})+8NaOH(1600\text{ aq.})\rightarrow 2Na_2CrO_4\text{ aq.}+4NaOH\text{ aq.}$+50·328 Cals. at 18°. W. G. Mixter gave for the heat of formation : $Cr+3Na_2O_2=Na_2CrO_4+2Na_2O$+158·8 Cals. ; $Cr_2O_{3\text{cryst.}}+3Na_2O_2=2Na_2CrO_4+Na_2O$+108·0 Cals. ; and (CrO_3,Na_2O)=77·0 Cals. M. Berthelot found for the heat of soln., Na_2CrO_4 with 360 to 720 mols of water, 2·2 Cals. at 10·5° ; $Na_2CrO_4.4H_2O$ with 650 mols of water, —7·6 Cals. at 11° ; and $Na_2CrO_4.10H_2O$ with 760 mols of water, —15·8 Cals. at 10·5°. Accordingly, the heat of hydration is $(Na_2CrO_{4\text{solid}},10H_2O_{\text{liquid}})$=18·0 Cals. at 10·5° ; and the heat of fusion of the decahydrate is —12·3 Cals. at 10·5°, and —13·4° Cals. at 23°. A. Heydweiller found the eq. conductivity, λ mhos, at 18° for 0·1066N-, 0·533N-, 1·066N-, and 4·264N-soln. to be, respectively, 81·84, 65·73, 56·96, and 29·05. R. Lenz, and H. C. Jones and H. P. Bassett made some observations on this subject, and C. Watkins and H. C. Jones gave for the mol. conductivity, μ mhos, for a mol of salt in v litres of water :

v	. .	4	8	16	32	128	512	1024
μ	0° .	74·76	83·56	90·74	98·16	110·40	118·32	114·60
	15° .	113·4	125·3	137·8	148·6	168·4	176·2	173·6
	25° .	—	156·5	171·3	185·1	206·7	219·5	216·9
	35° .	—	187·9	207·6	224·3	252·2	270·1	262·3

The percentage ionizations at 0° and 35° are :

v . . .	4	8	16	32	128	512
0° . . .	63·2	70·6	76·7	82·9	93·3	100·0
35° . . .	—	69·6	76·8	83·0	93·4	100·0

A. Berthoud observed no maximum in the conductivity curve. P. Düllberg studied the electrometric titration with hydrochloric acid. For the electrolysis of soln. of the chromate, *vide infra*, sodium dichromate. H. Ollivier studied the paramagnetism of the salt. H. Stamm measured the solubility of the salt in aq. ammonia, and found that soln. with 0 and 3·3079 mols NH_3 per 100 grms. of water dissolve 0·3595 and 0·1147 mol Na_2CrO_4, respectively. B. Neumann and C. Exssner studied the conversion of sodium chromate to dichromate on aq. soln. by carbon dioxide under press. J. F. John, and H. Moser said that the decahydrate is sparingly soluble in alcohol ; C. A. L. de Bruyn found 100 grms. of absolute methyl alcohol dissolve 0·345 grm. of Na_2CrO_4 at 25° ; and A. Naumann observed the salt to be insoluble in acetone. F. E. Brown and J. E. Snyder observed no reaction with boiling vanadium oxytrichloride and anhydrous sodium chromate.

L. Kahlenberg and W. J. Trautmann observed no reaction when the chromate is mixed with silicon and heated in a hard glass tube by a bunsen burner, but a strong reaction occurs when heated by a Méker burner. J. Zehenter precipitated **ammonium sodium chromate,** $(NH_4)NaCrO_4.2H_2O$, by adding alcohol to a mixed soln. of ammonium chromate and sodium carbonate; and G. N. Wyrouboff, from a mixed soln. of ammonium and sodium chromates. The rhombic, prismatic crystals are said to be isomorphous with the corresponding sulphate, the axial ratios are $a : b : c = 0{\cdot}4780 : 1 : 0{\cdot}8046$; the optical character is negative; and the optic axial angles for red and green light respectively are $2H_a = 93° \ 15'$ and $80° \ 15'$; $2H_0 = 108° \ 0'$ and $129° \ 30'$; and $2V = 83° \ 52'$ and $70° \ 56'$. According to J. Zehenter, the sp. gr. is 1·842 at 15°. The salt decomposes between 150° and 180° with the evolution of water and ammonia. The aq. soln. made just turbid with alcohol decomposes in light.

According to A. Raimondi,[4] the yellow mineral **tarapacaite** from the province of Tarapaca, Chili, occurs in the midst of the variety of soda-nitre called *caliche azufrado.* It is essentially a **potassium chromate,** K_2CrO_4, mixed with a little sodium chloride, nitrate, and sulphate, and potassium sulphate. I. Domeyko also observed its occurrence in the desert of Atacama, Chili. The preparation of potassium chromate has been discussed in connection with the extraction of chromium. T. Thomson, and J. von Liebig and F. Wöhler obtained it from the soln. obtained by neutralizing potassium dichromate with the carbonate. J. von Liebig and F. Wöhler converted chromic oxide into chromate by ignition with potassium chlorate; and V. Kletzinsky, fused potassium dichromate with the nitrate. N. J. Berlin purified the chromate by treating a soln. of the dichromate with a soln. of barium chromate in chromic acid; evaporated to dryness a mixture of the filtrate with an excess of potassium carbonate; and crystallized the product from aq. soln. until it was nearly free from alkali carbonate; digested the aq. soln. with silver chromate; and crystallized and recrystallized the chromate from the filtrate by spontaneous evaporation.

No hydrates are formed under ordinary conditions. Observations on the solubility of potassium chromate were made by T. Thomson, A. Michel and L. Krafft, H. Moser, M. Alluard, A. E. Nordenskjöld and G. Lindström, A. Étard, C. von Hauer, W. Kohlrausch, P. Kremers, M. Amadori, H. Schiff, K. F. Slotte, I. Koppel and E. Blumenthal, F. Flöttmann, and F. A. H. Schreinemakers. The general results show that the percentage solubility, S, is:

	−11·33°	−5·75°	0°	10°	20°	40°	60°	80°	100°	105·8°
S .	23·1	36·6	36·7	37·9	38·6	40·1	42·1	42·9	44·2	47·0

F. Flöttmann found the solubility at 15°, 20°, and 25° to be 2·725, 2·764, and 2·799 mols per litre, or 38·49, 38·94, and 39·38 per cent., respectively. The eutectic temp., ice and K_2CrO_4 is, according to L. C. de Coppet, —11·30° with 36·6 per cent. of salt; according to F. Guthrie, —11·00° and 36·3 per cent. of salt; and, according to I. Koppel and E. Blumenthal, at —11·70 and 35·3 per cent. of salt.

E. H. Riesenfeld and A. Wesch treated a conc. aq. soln. of $K_5[(CrO_4)_2Cy_5).5H_2O$ with alcohol; a red oil is precipitated. This is separated and covered with alcohol, and allowed to stand for some days in a calcium chloride desiccator, and purified by recrystallization. The analysis agrees with the *tetrahydrate,* $K_2CrO_4.4H_2O$. The pale yellow prisms gradually lose water, and they are slightly hygroscopic. The aq. soln. is neutral, and it is darker than that of ordinary potassium chromate, and paler than the dichromate.

The ternary system: $K_2O–CrO_3–H_2O$ at 30° was studied by F. A. H. Schreinemakers, who found for the percentage solubilities:

CrO_3 . . .	0	0·18	5·6	20·67	10·43	46·46
K_2O . . .	47	34·6	20·58	19·17	4·91	3·25
Solids		$KOH.2H_2O$	K_2CrO_4		$K_2Cr_2O_7$	
CrO_3 . . .	44·46	47·65	49·73	55·83	63·14	62·28
K_2O . . .	3·25	2·67	2·25	0·87	0·56	—
Solids		$K_2Cr_3O_{10}$		$K_2Cr_4O_{13}$	CrO_3	

The results are plotted in Fig. 36; where the solubility curve *ab* has the solid phase CrO_3; *bc*, potassium tetrachromate; *cd*, trichromate; *de*, dichromate; *ef*, chromate; and *fg*, $KOH.2H_2O$. I. Koppel and E. Blumenthal's results at 0°, 30°, and 60° are summarized in Figs. 37, 38, and 39. As before, *ab* represents the region when the solid phase is CrO_3; *bc*, $K_2Cr_4O_{13}$; *cd*, $K_2Cr_3O_{10}$; *de*, $K_2Cr_2O_7$; *ef*, K_2CrO_4; and *fg*, $KOH.4H_2O$ at 0°; $KOH.2H_2O$ at 30°; and $KOH.H_2O$ at 60°. The results are collected together in the model, Fig. 41, where the area gg_0f_0f refers to the hydrates of potassium hydroxide; f_0fee_0, to K_2CrO_4; e_0edd_0, to $K_2Cr_2O_7$; d_0dcc_0, to $K_2Cr_3O_{10}$; c_0cbb_0, to $K_2Cr_4O_{13}$; b_0baa_0, to CrO_3; $gfedcbaO$, to ice; and the area $g_0f_0E'_0e_0E_0d_0c_0b_0a_0(O_0)$, to the region where the vap. press. is 760°. $E'E'_0$ and EE_0 are eutectic lines. The b.p. for f_0 is 109°; E'_0, 105° 8°; e_0, 106·8°; E_0, 104·8°; d_0, 114·0°; and a_0, 127·0°. W. Herz and F. Hiebenthal found the solubility of potassium chromate, *S*, in the presence of *n*-normal soln. of various salts:

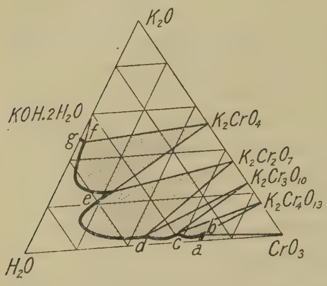
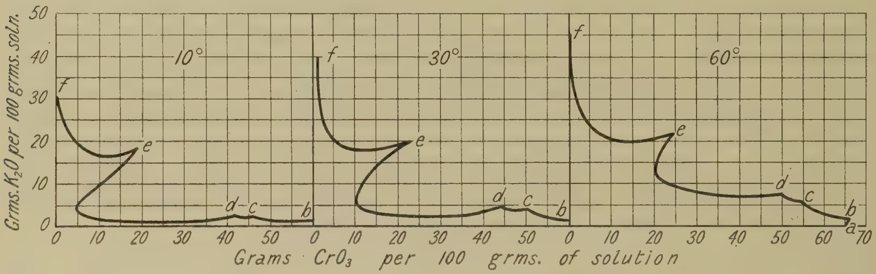


FIG. 36.—Equilibrium Diagram for the Ternary System: K_2O–CrO_3–H_2O at 30°.



FIGS. 37, 38, and 39.—Solubility of Potassium Chromate in Solutions of Chromic Acid.

NaCl	*n* .	0	0·42	0·86	1·73	2·59	3·30	3·40	4·25
	S .	8·35	8·11	7·71	6·51	5·46	4·79	4·57	4·49
KCl	*n* .	0·40	0·46	1·31	1·72	2·18	2·70	—	—
	S .	7·76	7·69	6·48	5·89	5·24	4·75	—	—
KBr	*n* .	0·41	0·82	1·24	1·78	2·19	2·70	—	—
	S .	7·56	6·91	6·26	5·50	5·00	4·38	—	—
$MgCl_2$	*n* .	0·42	0·86	1·73	2·27	2·76	3·26	—	—
	S .	7·58	6·11	4·30	2·74	1·30	1·04	—	—
NH_4Cl	*n* .	0·45	0·83	1·81	2·34	2·73	3·76	4·51	—
	S .	7·68	6·92	5·58	5·00	4·43	3·49	2·87	—

for NaCl, $S=8·770-1·24n$; for KCl, $S=8·287-1·31n$; for KBr, $S=8·129-1·39n$; for $MgCl_2$, $S=8·697-2·68n$; and NH_4Cl, $S=8·318-1·425n$.

The rhombic, bipyramidal crystals are pseudohexagonal, and, according to E. Mitscherlich, have the axial ratios $a:b:c=0·5694:1:0·7298$. W. Brendler gave $a:b:c=0·5694:1:0·7298$ for crystals of tarapacaite. Observations on the crystals of potassium chromate were also made by H. J. Brooke, H. Baumhauer, H. Topsöe and C. Christiansen, F. Corio, W. J. Grailich and V. von Lang, F. Corio, A. Hettich and A. Schleede, etc. The habit was found by H. de Sénarmont to be tabular when the crystals are grown in a soln. of sodium carbonate; but J. W. Retgers said that the crystals are those of $K_3Na(CrO_4)_2$, and not of potassium chromate. R. Marc and W. Wenk found that the velocity of crystallization of fused potassium chromate is three-fourths the speed of that of fused potassium sulphate; O. Schott, that a soln. of the salt in molten potassium nitrate furnishes crystals with a habit different from that which later obtains; while O. Lehmann said that the habit of the crystals under these conditions is unchanged. The (010)- and (001)-cleavages are clear. O. Lehmann observed the development of cleavage planes as the solid is heated. K. Herrmann and co-workers found the X-radiograms of the rhombic bipyramidal crystals of potassium chromate have a simple lattice with four mols. per unit cell, with $a=7{\cdot}45$ A., $b=10{\cdot}3$ A.; and $c=5{\cdot}88$ A. E. Kochholm and N. Schönfeldt studied the isomorphism of this salt with potassium sulphate and selenate. H. Topsöe and C. Christiansen found that the optical character is negative, and the optic axial angle $2V=51°\ 40'$; and $2E=97°\ 30'$. W. J. Grailich and V. von Lang gave $2E=92°$. A. des Cloizeaux gave $2E=100°\ 32'$ for red-light, 95° 40′ for blue-light, and 93° 10′ for blue-light. H. de Sénarmont, and W. J. Grailich and V. von Lang found that the optic axial angles increase with a rise of temp. L. Stibing gave for the axial ratios of solid soln. of potassium sulphate and chromate with 0·5 molar per cent. of potassium chromate $a:b:c=0{\cdot}5727:1:0{\cdot}7434$; 0·19 per cent., 0·5723 : 1 : 0·7436; 2·44 per cent., 0·5719 : 1 : 0·7445; 8·26 per cent., 0·5715 : 1 : 0·7444; 38·47 per cent., 0·5712 : 1 : 0·7418; 90·59 per cent., 0·5704 : 1 : 0·7381; and 100 per cent. 0·5696 : 1 : 0·7351 when potassium sulphate alone has 0·5727 : 1 : 0·7418. The topic axes of potassium chromate are $\chi:\psi:\omega=3{\cdot}9708:4{\cdot}0113:5{\cdot}1244$, when those of potassium sulphate are 3·8576 : 3·8805 : 4·9968. E. Pietsch and co-workers studied the attack of the edges and corners of the crystals by sulphuric acid.

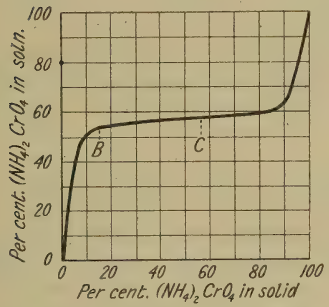


Fig. 40.—Solubility of the Binary System: $(NH_4)_2CrO_4$–K_2CrO_4 at 25°.

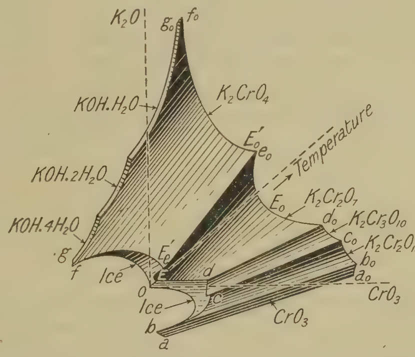


Fig. 41. — Equilibrium Model for the System: K_2O–CrO_3–H_2O at different Temperatures.

T. Ishikawa studied the system: $(NH_4)_2SO_4$–$(NH_4)_2CrO_4$–K_2CrO_4–K_2SO_4; and S. Araki found the solubility curves for the system $(NH_4)_2CrO_4$–K_2CrO_4–H_2O at 25°. The curve has two branches with two series of solid soln., and a gap with between 16·75 and 55·50 molar per cent. of ammonium chromate, *BC*, Fig. 40. According to S. F. Schemtschuschny, the cooling curve of potassium chromate exhibits two transition points, one at 984° corresponding with the crystallization of the molten liquid, and another at 679° corresponding with the conversion of the solid into another crystalline form, Fig. 42. This transition is attended by a change of the yellow into a red salt on heating. E. Groschuff said that this change of colour is evident at 260°, and that the change is gradual so that

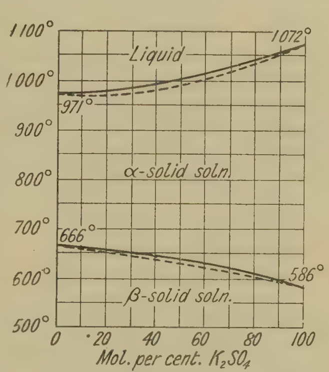


Fig. 42.—The Effect of Potassium Sulphate on the Freezing and Transition Points of Potassium Chromate.

it does not appear to be connected with the transition point. F. Rinne observed the reversibility of the colour changes when the salt is heated by the bunsen flame. E. Groschuff placed the transition temp. at 666°; and A. Hare, at 660°. The α-form is stable above 666°, and is completely miscible with the hexagonal form of potassium sulphate so that the high temp. form is itself hexagonal; as the ordinary or β-form of potassium chromate is completely miscible with the β-form of potassium sulphate. Neither the f.p. curve, nor the transition curves, Fig. 42, shows a maximum or minimum. M. Amadori obtained a similar equilibrium diagram. Yellow potassium chromate, stable at ordinary temp., is isomorphous with potassium sulphate, and, therefore, cannot be separated from that salt by fractional crystallization. W. von Behren and J. Traube studied the dissolution and crystallization of the salt. R. Kollmann, G. Tammann and A. Sworykin, E. Mitscherlich, P. Groth, C. F. Rammelsberg, and J. W. Retgers said the salt is isomorphous with potassium sulphate, selenate, and permanganate. G. Tammann discussed the protection of one salt by another in the case of solid soln. of potassium chromate and sulphate in a soln. of the sulphate. H. Rose observed that a mixture of eq. proportions of sodium sulphate and potassium chromate yields a brittle mass which dissolves in water and yields crystals resembling potassium sulphate. The optical properties of solid soln. of potassium sulphate and chromate were examined by L. Stibing, G. N. Wyrouboff, and E. Mallard; and the solubility and sp. gr. of soln. of the two salts were examined by M. Herz, A. Fock, and M. Amadori. G. Meyer studied the application of the partition law to the solid soln. of potassium sulphate and chromate in aq. soln. M. Amadori gave for the solubility of potassium chromate in the presence of the sulphate:

K_2SO_4	69·88	58·78	40·86	27·65	13·53	7·51	4·35	0
K_2CrO_4	0·00	22·44	75·34	140·7	266·5	315·7	324·5	332·3

so that the curve is in agreement with the results obtained by A. Fock, but not with those of M. Herz. The mutual solubility of the two salts in the solid state is complete; and the more soluble salt is always in greater proportion in the soln. than in the crystals. The solubility curve of potassium chromate and molybdate is similar. L. Stibing gave for mixtures of potassium sulphate and chromate in soln. and solid soln., when the composition is expressed in molar per cent. K_2CrO_4 per litre:

Soln.	0·0741	0·2642	0·6281	0·7543	1·0197	1·8450	2·6867
Solid	0·0053	0·02337	0·0294	0·0355	0·1603	0·1892	0·5795

A. Fock's results at 25° are summarized in Fig. 42. T. V. Barker studied parallel overgrowths on alkali sulphates and chromates. H. E. Buckley studied the effect of chromates on the crystallization of sodium chlorate.

T. Thomson gave 2·612 for the sp. gr. of potassium chromate; C. J. B. Karsten, 2·6402; H. Kopp, 2·705; L. Playfair and J. P. Joule, 2·711 to 2·72309 at 4°; S. Holker, 2·678 at 15·5°; H. Schiff, 2·691; F. Stolba, 2·7343; H. G. F. Schröder, 2·719 to 2·722; J. W. Retgers, 2·727; A. Cavazzi, 2·691 at 15°; B. Gossner, 2·741; J. L. Andreae, 2·7319 at 18°; and W. Spring,

	0°	10°	20°	40°	60°	80°	100°
Sp. gr.	2·740	2·737	2·735	2·729	2·723	2·711	2·7095

W. Spring, and L. Stibing observed the sp. gr. of solid soln. of potassium chromate and sulphate, and the values calculated by the additive rule:

K_2CrO_4	0·5080	1·2065	2·7093	9·3837	40·5333	91·5450 per cent.
Sp. gr. (Cals.)	2·6664	2·6669	2·6680	2·6732	2·6959	2·7345 ,,
Sp. gr. (Obs.)	2·666	2·667	2·668	2·673	2·696	2·735 ,,

F. Fouqué found that the sp. gr. of aq. soln. of potassium chromate with 0·97, 3·35, and 20·57 grms. of salt per 100 grms. of water are respectively 1·0077, 1·0268, and 1·1533 at 0°/4°; 1·0065, 1·0257, and 1·1500 at 16·4°/4°; 0·9836, 1·0013, and

1·1165 at 75·5°/4°; and 0·9679, 0·9861, and 1·1065 at 99°. Observations were also made by P. Kremers, R. L. Datta and N. R. Dhar, P. F. Gaehr, and A. Heydweiller. For soln. of the following percentage composition, at 195°, H. Schiff, and G. T. Gerlach found:

K_2CrO_4 .	1	5	10	15	20	25	30	35	40 per cent.
Sp. gr. .	1·0080	1·0492	1·0837	1·1287	1·1765	1·2274	1·2808	1·3386	1·3991

H. Schiff represented his results for soln. with p per cent. of K_2CrO_4 by $S=1+0·008p+0·0_43324p^2+0·0_64048p^3$ at 19·5°. F. Flöttmann found the sp. gr. of soln. sat. at 15°, 20°, and 25° to be, respectively, 1·3749, 1·3785, and 1·3805. A. Cavazzi measured the expansion in vol. which occurs when potassium chromate is dissolved in water. K. F. Slotte found the sp. gr. of a soln. with 24·26 per cent. K_2CrO_4 at 18° to be 1·2335; and the viscosity (water 100), 133·3 at 10°; 106·5 at 20°; 87·9 at 30°; and 74·3 at 40°. The drop weight of the salt just above its m.p. was found by I. Traube to be 238 mgrms. (water 100). J. Wagner found for N-, 0·5N-, 0·25N-, and 0·125N-soln. the viscosity (water unity) 1·1133, 1·0528, 1·0224, and 1·0116 respectively. L. J. Simon mixed equimolar soln. of chromic acid and potassium or sodium hydroxide, and found that discontinuities occur in the viscosity curves when the composition of the soln. corresponds with either the normal chromates or the dichromates, the precise form of the curves depending on whether the relative proportion of the two soln. is taken as the abscissa or the viscosities for soln. of equimolar conc. are compared. Except in high concentrations, the viscosities of eq. soln. of sodium chromate and sodium sulphate, and of potassium chromate and potassium sulphate are identical, and it is concluded that within certain conc. limits, isomorphous solutes produce the same change in the viscosity of the aq. solvent. T. Graham made some observations on the diffusion of potassium chromate into a soln. of potassium acetate; and J. C. G. de Marignac, on the diffusion in the presence of potassium carbonate, or nitrate. Experiments on the diffusion of soln. of chromic acid were also made by F. Rudorff, and H. de Vries. G. Jander and A. Winkel gave 0·77 for the diffusion coeff. of the anion. W. Spring found that with the vol. of potassium chromate unity at 0°, the vol., v, at different temp. is:

	10°	20°	30°	40°	60°	80°	100°
v .	1·001064	1·002114	1·003140	1·004228	1·006439	1·009023	1·011344

which makes the coeff. of cubical expansion 0·00011344 between 0° and 100°, a result very close to that obtained by L. Playfair and J. P. Joule; J. L. Andreae gave 0·000101 between 18° and 56°. W. Spring also found that the coeff. of cubical expansion is very close to that of ammonium and rubidium sulphates. H. Kopp observed the sp. ht. of the crystalline salt to be 0·189 between 18° and 47°; H. V. Regnault gave 0·1850 between 17° and 98°; and F. E. Neumann, 0·1840. J. C. G. de Marignac gave for the sp. ht. of soln. of a mol of potassium chromate in 50, 100, and 200 mols of water between 20° and 51°, respectively 0·8105, 0·8896, and 0·9407; while H. Faasch gave for 0·499N-, 0·990N-, 1·994N-, and 3·986N-K_2CrO_4, respectively 0·939, 0·898, 0·810, and 0·703 at 18°. The subject was discussed by N. de Kolossowsky. J. J. Berzelius observed that the lemon-yellow salt becomes bright red when heated, but undergoes no further change; it is liable to decrepitate violently before fusion at a red-heat, and emits a green light during fusion; and the molten salt, said G. Magnus, crystallizes as it cools. H. le Chatelier first gave 975° for the m.p., and later,

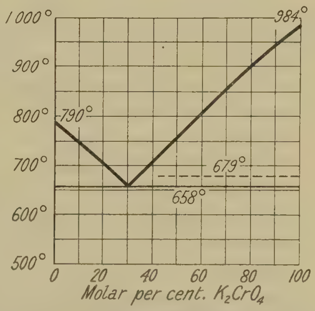


FIG. 43.—Freezing-point Curve of the Mixtures of K_2CrO_4–K_2SO_4.

940°; S. F. Schemtschuschny, 984°; E. Groschoff, 971°; and M. Amadori, 978°. D. F. Smith and F. A. Hartgen studied this subject. For the transition temp., *vide supra.* H. le Chatelier, E. Groschuff, and M. Amadori studied the m.p. of mixtures of potassium sulphate and chromate—*vide* Fig. 43—a continuous series of solid soln. is formed. M. Amadori obtained continuous series of solid soln. with potassium chromate and potassium molybdate or tungstate. S. F. Schemtschuschny studied the m.p. of the binary system K_2CrO_4–KCl, and found a typical V-curve with a eutectic at 658°, and 31·5 molar per cent. of K_2CrO_4; no solid soln. are formed on the potassium chloride branch of the curve, but the other branch shows that solid soln. are formed with mixtures containing about 4 molar per cent. of potassium chloride, Fig. 43. F. Guthrie found that a mixture of potassium chromate and nitrate has a eutectic at 295° and 96·2 per cent. of the nitrate; for mixtures of potassium chromate and dichromate, *vide infra.* The lowering of the f.p. of soln. of w grms. of K_2CrO_4 in 100 grms. of water, was measured by L. C. de Coppet, and F. Rüdorff; while I. Koppel and E. Blumenthal gave:

K_2CrO_4 .	4·53	6·12	26·99	31·33	42·04	54·57
Lowering f.p.	0·99°	1·2°	4·3°	5·7°	7·12°	11·37°

For the eutectic temp., *vide supra.* G. Tammann gave for the lowering of the vap. press. for soln. with w grms. of K_2CrO_4 per 100 grms. of water,

K_2CrO_4 . . .	10·93	14·29	26·63	34·89	46·99	53·28
Lowering v.p. .	18·0	22·7	40·4	52·1	73·7	84·1 mm.

I. Bencowitz and H. T. Hotchkiss, and F. M. Raoult made some observations on this subject. According to M. Alluard, the b.p. of a sat. soln. of the chromate is 104·2° at 718 mm.; according to P. Kremers, 107°; and according to I. Koppel and E. Blumenthal, 105·8° at 760 mm. A. Hare found the heat of the polymorphic transformation of potassium chromate at 660° to be 2·45 Cals. per mol. R. Lorenz and W. Herz studied some relations between the b.p. and critical temp. The heats of neutralization given by M. Berthelot are $(CrO_{3aq.},2KOH_{aq.})=30·4$ Cals. at 12°; with the solid compounds, 95·6 Cals.; with $K_2Cr_2O_7$ (in 12 litres) and 2KOH (in 4 litres), M. Berthelot gave 23·6 Cals., and P. Sabatier, 23·0 Cals.; and for H_2CrO_4 (in 8 litres) and 2KOH (in 4 litres). M. Berthelot gave 27·738 Cals., and P. Sabatier, 25·4 Cals. M. Berthelot also gave for $(2Cr(OH)_{3\text{precipitated}},4KOH_{aq.},3O)=61·4$ Cals. at 8°; and for solid hydroxide and chromate, 101·9 Cals. F. Morges gave −5·254 Cals. for the heat of soln. in 543 mols of water at 19·5°.

H. Topsöe and C. Christiansen gave for the index of refraction, 1·7131 for the *C*-line; 1·7154 for the *D*-line; and 1·7703 for the *F*-line. E. Mallard gave for red-light, $\alpha=1·6873$, $\beta=1·722$, and $\gamma=1·7305$. F. Fouqué, and R. L. Datta and N. R. Dhar measured the refractive indices of aq. soln.; and A. Heydweiller gave for the *D*-line at 18°:

K_2CrO_4 . .	0·1*N*-	0·2*N*-	0·5*N*-	1·0*N*-	2·0*N*-	4·0*N*-
μ . . .	1·33529	1·33732	1·34335	1·35305	1·37188	1·40709

F. Flöttmann found the index of refraction of soln. sat. at 15°, 20°, and 25° to be respectively 1·43267, 1·43276, and 1·43288. H. Fromherz studied the absorption spectrum. L. R. Ingersoll found Verdet's constant for the electromagnetic rotatory power for light of wave-length 0·6, 0·8, 1·0, and 1·25μ to be respectively 0·0092, 0·0060, 0·0041, and 0·0026 for soln. of sp. gr. 1·372. T. Thomson said that one part of the salt imparts a distinct yellow colour to 40,000 parts of water. The spectroscopic observations of H. Becquerel, W. Böhlendorff, A. Étard, F. Grunbaum, J. M. Hiebendaal, J. H. Jones and W. W. Strong, E. Viterbi and G. Krausz, O. Knoblauch, P. Sabatier, J. L. Soret, H. Settegast, A. M. Taylor, T. Aden, N. R. Tawde and E. R. Paranjpe, E. Jander, and K. Vierordt have been previously discussed. C. Schaefer and M. Schubert found in the ultra-red spectrum a well-defined maximum at 11·16μ with soln. of potassium chromate, and at 11·2μ with soln. of potassium sodium chromate. H. von Halban and K. Siedentopf studied the absorption of light in cells of potassium chromate and hydroxide soln., and soln. of potassium chromate and copper sulphate in aq. ammonia. A. E. Lindh, D. Coster, and O. Stelling studied the X-ray spectrum; and D. M. Yost, the absorption of X-rays. I. Plotnikoff and M. Karshulin measured the absorption spectrum and the region of photochemical sensitivity for soln. of potassium chromate in colloidion films—with methyl alcohol as acceptor. A. Kailan found that an aq. soln. of potassium chromate is reduced by radium rays more slowly than potassium dichromate. E. Montignie observed that after exposure to ultra-violet light, potassium chromate affects a photographic plate.

J. A. Fleming and J. Dewar found that the dielectric constant of water is raised a little by potassium chromate, and at —88·5°, the dielectric constant of the frozen mixture is between 3 and 10—when with ice alone, the constant is 2·5. W. Schneider studied the piezoelectric effect; P. Walden, and A. Heydweiller, the electrical conductivity of aq. soln. P. Walden gave for the eq. conductivity, λ mhos, at 8°, with a gram-equivalent of the salt in v litres,

v . . .	32	64	128	256	512	1024
λ . . .	129·6	136·3	141·3	145·5	148·3	150·4

H. C. Jones and C. A. Jacobson measured the molar conductivity, μ mhos, between 0° and 35°, and A. M. Clover and H. C. Jones, between 35° and 65°, for a mol of the salt in v litres; and calculated values for the percentage ionization, α;

v	. .	2	8	16	32	128	512	1024	2048
μ	0° . .	102·9	118·6	125·6	132·8	149·3	156·8	160	161·4
	125° .	136·6	161·9	174·3	185·2	204	219	223	225
	25° .	176·6	209	228	242	270	290	294	298
	35° .	211	251	273	290	323	349	352	356
	50° .	266	317	—	366	415	442	—	—
	65° .	316	381	—	445	429	548	—	—
α	0° .	63·7	73·5	77·8	82·5	92·5	97·2	99·1	100·0
	35° .	59·6	70·4	76·6	81·4	90·6	98·1	98·8	100·0

Conductivity observations were also made by R. Lenz, and E. Bouty. N. R. Dhar said that electrical conductivity and coagulation experiments agree that in soln. the dichromate is in part present as $KHCrO_4$. F. Morges observed that in the electrolysis of an aq. soln. of the chromate, potassium hydroxide accumulates about the cathode, and the oxygen given off at the anode forms dichromate—*vide supra*. chromic acid. As indicated in connection with chromic acid, calculations on the degree of ionization are unsatisfactory on account of the conversion of chromates to dichromates in aq. soln. J. Lundberg's observations on the hydrolysis of these soln. were indicated in connection with chromic acid. The aq. soln. has an alkaline reaction towards lacmoid, litmus, and phenolphthalein, and observations on this subject were made by M. M. Richter, R. T. Thomson, and J. A. Wilson. H. M. Vernon estimated the degree of ionization from the colour. G. Baborovsky studied the electrolytic reduction of the salt; and P. Düllberg, the electrometric titration with hydrochloric acid. L. A. Welo gave $0{\cdot}04\times10^{-6}$ for the magnetic susceptibility. G. Gore electrolyzed fused potassium chromate and obtained a deposit on the cathode.

J. Obermiller measured the hygroscoposity of the crystals. H. Moser said that potassium chromate is not decomposed when heated to redness—*vide supra*, chromium trioxide. W. Ipatieff and co-workers found that hydrogen under a press. of 200 atm. reduces soln. of potassium chromate; and with a soln. of potassium chromate and sulphuric acid, $Cr_2(SO_4)_3.Cr_2O_3.K_2O.H_2O$ is formed. G. Gore observed that the salt becomes red in compressed hydrogen chloride, but in liquid hydrogen chloride it is neither changed nor dissolved. A. C. Robertson studied the action of potassium chromate on hydrogen dioxide: $2K_2CrO_4+H_2O_2=K_2Cr_2O_7$

$+2KOH+O$—*vide supra,* potassium dichromate; and *vide supra,* chromic acid. G. Grasser and T. Nagahama found that the reduction with many reducing agents is incomplete unless an acid be present. J. W. Thomas found that the salt is decomposed by dry hydrogen chloride forming potassium chloride and dichromate; the dichromate is then converted into chromium trioxide, and this is then reduced to a brown chromic oxide without forming chromyl chloride. M. Bobtelsky studied the oxidation of conc. hydrochloric acid by potassium chromate. W. B. Morehouse found the X-ray absorption of the system: $K_2Cr_2O_7+16KI+14HCl \rightarrow 8KCl +2CrCl_3+4I_2+8KI+7H_2O$ is 0·25 per cent. greater after the reaction than it is before. E. Ramann and H. Sallinger measured the precipitation ratio, *i.e.* the ratio in which silver divides itself between the iodate and chromate in the reaction: $K_2CrO_4+2AgIO_3=2KIO_3+Ag_2CrO_4$. J. L. Lasssaigne found that when heated with sulphur, chromic oxide and potassium sulphate and sulphide are formed: $8K_2CrO_4+(3n+5)S=5K_2SO_4+3K_2S_n+4Cr_2O_3$; initially, said O. Döpping, some thiosulphate is produced. K. Brückner said that when the mixture of chromate and sulphur is heated for a short time, potassium sulphide and thiosulphate are formed, and afterwards potassium sulphate and polysulphide as well as chromic sulphide and oxide. As the heating continues, the sulphide is slowly oxidized, and the end-products are potassium sulphate, and chromic oxide with traces of chromates, and chromium sulphide. J. B. Senderens represented the reaction when the aq. soln. is boiled with sulphur, by $6K_2CrO_4+15S+9H_2O=6Cr(OH)_3 +5K_2S_2O_3+K_2S_5$; and O. Döpping, the reaction with potassium pentasulphide, by $8K_2CrO_4+2K_2S_5+5H_2O=5K_2S_2O_3+10KOH+4Cr_2O_3$. The reaction between the heated salt and dry hydrogen sulphide was found by W. Müller to furnish water, potassium and chromium sulphides and chromic oxide; with an aq. soln. of the chromate, saturated with sodium hydroxide, T. L. Phipson found that green chromic hydroxide is precipitated—*vide infra;* chromium sulphide. W. R. Hodgkinson and J. Young studied the action of dry sulphur dioxide on the salt. W. Müller represented the reaction between the heated salt and the vapour of carbon disulphide by $2K_2CrO_4+5CS_2=2K_2S_3+Cr_2S_3+4CO+CO_2+SO_2$. P. Berthier said that sulphur dioxide precipitates brown chromic chromate from an aq. soln. of potassium chromate. The precipitate then dissolves forming a green liquid containing potassium hydroxide, chromic oxide and sulphuric, sulphurous, and dithionic acids. P. Job found that 0·01 to $0{\cdot}001M$-K_2CrO_4, reacts with sulphuric acid, so that the reaction $CrO_4''+H^{\cdot}\rightleftharpoons HCrO_4'$ has an ionization constant $K=7\times10^{-5}$ at 15°. E. Pietsch and co-workers studied the surface conditions in the reaction between potassium chromate and sulphuric acid. E. C. Franklin and C. A. Kraus found the chromate to be insoluble in liquid ammonia. H. Stamm found that soln. with 0, 1·350, and 3·517 grms. of NH_3 per 100 grms. of water dissolve 0·3218, 0·0324, and 0·0036 mol of K_2CrO_4 respectively. R. C. Woodcock, and F. Mohr found that when the chromate is distilled with ammonium chloride and water, ammonia and potassium dichromate are formed. F. Santi found that ammonium chloride converts chromates to dichromates and dichromates to chromic acid; and E. Divers that chromates react with a soln. of ammonium nitrate in aq. ammonia. H. P. Cady and R. Taft observed that potassium chromate is appreciably soluble in phosphoryl chloride. J. T. Cooper observed that a yellow soln. of chromate gradually turns green in the presence of arsenic trioxide. H. Moser observed the decomposition of potassium chromate mixed with carbon and heated—potassium carbonate and chromic oxide are formed. E. Fleischer observed that the aq. soln. of the chromate attracts carbon dioxide from the atm. When the chromate is heated in a current of carbon monoxide, F. Göbel observed that chromic oxide is formed; and K. Stammer added that potassium carbonate, carbon dioxide, and potassium chromite are also produced. J. Jacobson found that when carbon, gun cotton, and other organic substances are soaked in a soln. of potassium chromate and dried, they burn more vigorously than before. F. W. O. de Coninck observed that 100 grms. of a soln. of glycol sat. at 15·4, contain 1·7 grms. of potassium chromate. A. Naumann found the chromate to be insoluble in benzonitrile, and in methyl acetate; and A. Naumann, and W. Eidmann, insoluble in acetone. It is also insoluble in alcohol. F. Göbel found that potassium chromate is partially decomposed when heated in carbon monoxide, and chromic oxide is formed. G. Stadnikoff studied the adsorption of potassium chromate by aniline-black. S. Glasstone and co-workers studied the effect of the chromate on the solubility of ethyl alcohol. F. Tassaert observed that when the chromate is heated with acetic acid and alcohol, it is partly transformed into potassium and chromic acetates. According to F. Tassaert, many acids—sulphuric, hydrochloric, nitric, and acetic acids—abstract half the alkali, and form potassium dichromate, which, if the soln. be sufficiently concentrated, is precipitated—*vide supra*, chromium trioxide. E. Schweizer said that carbonic acid acts similarly, and F. Margueritte, boric acid; but F. Mohr added that boric and silicic acids, and potassium hydrocarbonate do not act in this way, but that formic, acetic, butyric, and valerianic acids do transform chromate into dichromate. If soln. of the potassium salts of one of these four acids be evaporated with potassium dichromate, potassium chromate is formed. F. Mohr added that potassium hydrocarbonate acts similarly. According to E. Schweizer, a soln. of potassium dichromate with sodium stearate precipitates stearic acid; benzoic acid forms potassium benzoate and dichromate when treated with potassium chromate, and when the soln. is evaporated, potassium chromate and benzoic acid are reformed. A soln. of sodium benzoate and potassium dichromate does not yield chromate on evaporation. Salicylic acid behaves like benzoic acid. Normal potassium urate reacts with the chromate forming uric acid and potassium dichromate. M. Berthelot, and P. Sabatier studied the reaction of the chromate with acids. According to J. W. Döbereiner, a soln. of barium hydroxide gives a quantitative precipitate of barium chromate. According to L. Meyer, an aq. soln. of potassium chromate in contact with crystals of copper sulphate, silver nitrate, mercurous nitrate, or mercuric chloride forms potassium dichromate and a little basic chromate is precipitated; lead acetate is not changed; cobaltous chloride gives a precipitate—*vide supra*, reactions of chromates. K. W. Floroff studied the reaction $BaSO_4+K_2CrO_4=K_2SO_4+BaCrO_4$. L. Kahlenberg and W. J. Trautmann observed no reaction when the chromate mixed with silicon is heated in a hard glass tube by a bunsen burner, but there is a strong reaction when heated by a méker burner. A. C. Robertson represented the reaction with vanadic acid: $2K_2CrO_4+H_2O_2+HVO_3=K_2Cr_2O_7+2KOH+HVO_4$. R. F. Reed and S. C. Horning showed that potassium chromate in aq. soln. is absorbed by zinc, possibly as potassium or zinc chromate.

S. W. Johnson cooled by a freezing mixture a hot soln. of potassium dichromate in conc. ammonia, and obtained crystals of **ammonium potassium chromate,** $(NH_4)KCrO_4$; E. Kopp obtained the same salt by evaporating the soln. over caustic alkali. The rhombic, pale sulphur-yellow prisms are isomorphous with potassium sulphate. E. Maumené said that the salt turns brown at 240° owing to the formation of the chromate of a base N_2H_6O, and that the salt is completely decomposed at 270° leaving residual chromic oxide. P. Sabatier gave 10·6 Cals. for the heat of formation from a soln. of potassium dichromate; or 15·5 Cals. from the solid salts; the heat of soln. for 173·4 grms. of salt in 40 times its weight of water at 17° is $-5·3$ Cals. S. W. Johnson found that the salt loses ammonia when exposed to air, and when the soln. is boiled or evaporated there remains potassium dichromate. E. Kopp said that sodium thiosulphate has no action in the cold, but when heated, chromic chromate is formed. A. Étard's analysis indicates that the salt is monohydrated; but S. W. Johnson's analysis shows that the salt is anhydrous. J. Zehenter prepared $2(NH_4)_2CrO_4.3K_2CrO_4$, by adding an eq. of potassium carbonate to a conc. soln. of ammonium dichromate, and precipitating with alcohol. The sulphur-yellow needles have a sp. gr. 2·403 at 15°. They are stable when dry. H. Traube prepared **lithium potassium chromate,** $LiKCrO_4$, in hexagonal or pseudo-hexagonal crystals isomorphous with the analogous sulphate; J. Zehenter gave 2·539 for the sp. gr. at 15°. H. Rose melted 2 parts of potassium dichromate and one of sodium carbonate; the cold mass dissolved in hot water deposits, on cooling, crystals of **potassium sodium chromate,** or *chromoglaserite,* or *chromatoglaserite,* $3K_2CrO_4.Na_2CrO_4$, or $K_3Na(CrO_4)_2$—the crystallization is attended by crystalloluminesce. J. Zehenter obtained the salt by evaporating a hot soln. of potassium dichromate neutralized with sodium carbonate; and C. von Hauer, by evaporating a mixed soln. of 3 mols of potassium chromate and one mol of sodium chromate. The yellow crystals were found by B. Gossner to be trigonal with the axial ratio $a:c=1:1{\cdot}2857$ and $\alpha=88°\ 28'$, there is a second variety in monoclinic crystals with $a:b:c=0{\cdot}5833:1:0{\cdot}8923$, and $\beta=90°\ 46'$. H. Steinmetz said that there is a gradual change in the chromate, $K_3Na(CrO_4)_2$, between 150° and 175° without appreciable change of vol. or coeff. of expansion. The sp. gr. is 2·719 at 15°; at 14°, 100 parts of water dissolve 64·2 parts of salt. According to J. Zehenter, the mother-liquor yields a hemihydrate, of sp. gr. 2·575 at 15°. It loses water at 150°; and 100 parts of water at 14° dissolve 66·4 parts of salt. E. Flach measured the f.p. of mixtures of sodium and potassium chromates, and the results are summarized in the upper curve of Fig. 44. The solid soln. of the two salts shows breaks in the cooling curve corresponding with the lower curve of Fig. 44. There are thus indications of the formation of the trigonal chromatoglaserite analogous to ordinary or sulphatoglaserite, $3K_2SO_4.Na_2SO_4$. This complex salt can form solid soln. to a limited extent with sodium chromate, so that during the cooling the hexagonal crystals of the solid soln. between 669° and 371° mostly split into simple chromates and solid soln. of chromatoglaserite and sodium chromate. The curve of mixtures of potassium and sodium chromates, previously fused together, shows a break corresponding with $K_3Na(CrO_4)_2$. Thus,

K_2CrO_4 .	0	10	50	70	78·3	90	100 per cent.
Sp. gr. .	2·765	2·766	2·767	2·767	2·768	2·751	2·740

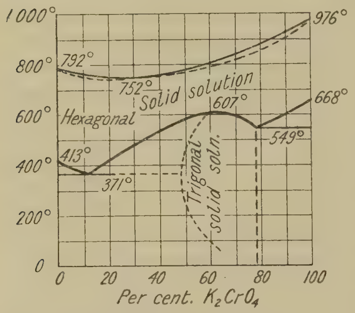


FIG. 44.—Equilibrium Diagram of the Binary System: Na_2CrO_4–K_2CrO_4.

The crystallographic data are summarized in Table III. The thermal diagram of mixtures of sulphato- and chromato-glaserites is shown in Fig. 45. The quaternary system: K_2CrO_4–Na_2CrO_4–Na_2SO_4–K_2SO_4, was studied by E. Flach and also the same system with water at 30°.

TABLE III.—CRYSTALLOGRAPHIC DATA OF POTASSIUM AND SODIUM SULPHATES AND CHROMATES.

	Mol. wt.	Sp. gr.	Mol. vol.	Axial ratios $a:b:c$	Topic parameters $\chi:\psi:\omega$
K_2SO_4 .	174·27	2·666	65·37	0·5727 : 1 : 0·7418	3·0688 : 5·3586 : 3·9750
$K_3Na(SO_4)_2$	166·22	2·696	61·65	0·5773 : 1 : 0·7450	3·0215 : 5·2334 : 3·8990
Na_2SO_4 .	142·07	2·683	52·95	0·4731 : 1 : 0·7996	2·4564 : 5·1922 : 4·1517
K_2CrO_4 .	194·20	2·740	70·88	0·5694 : 1 : 0·7298	3·1578 : 5·5452 : 4·0473
$K_3Na(CrO_4)_2$	186·15	2·768	67·25	0·5773 : 1 : 0·7423	3·1141 : 5·3737 : 4·0038
Na_2CrO_4 .	162·00	2·765	58·59	0·4643 : 1 : 0·7991	2·5096 : 5·4051 : 4·3193

L. Grandeau [5] prepared **rubidium chromate,** Rb_2CrO_4, by neutralizing a soln. of the dichromate with rubidium carbonate, and by melting chromic oxide with rubidium nitrate, or with rubidium carbonate in air. The spontaneous evaporation of the aq. soln. furnishes first a crop of crystals of the dichromate, and then the chromate. The aq. soln. has an alkaline reaction. According to J. Piccard, the yellow crystals are rhombic bipyramids with the axial ratios $a : b : c = 0{\cdot}5665 : 1 : 0{\cdot}7490$. The (001)-cleavage is marked. The optic axial angles found by G. N. Wyrouboff were $2H_0 = 73° 46'$ for red-light, and 76° 5′ for green-light; and $2H_0 = 146°$ for white light. The topical character is negative. J. W. Retgers, J. Piccard, and L. Grandeau said that the crystals are isomorphous with potassium chromate, sulphate, and selenate. T. V. Barker studied parallel overgrowths on alkali sulphates and chromates. F. A. H. Schreinemakers and H. Filippo found the percentage solubility, S, to be:

	−7°	0°	10·3°	20°
S .	36·6	38·2	40·2	42·4

	30°	40°	50°	60·4°
S .	44·1	46·1	47·4	48·9

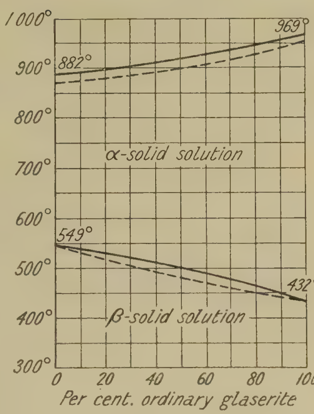


FIG. 45.—The Binary System of Sulphato- and Chromato-glaserites.

They also studied the ternary system: Rb_2O–CrO_3–H_2O at 30°; and found that with the composition of the soln. expressed in percentages:

CrO_3 . .	0	0·00	11·98	15·54	4·87	15·05
Rb_2O . .	60·56	56·82	27·99	28·55	4·60	3·45
Solids	$RbOH.2H_2O$	Rb_2CrO_4		$Rb_2Cr_2O_7$		

CrO_3 . .	15·05	24·92	14·29	58·69	63·07	62·28
Rb_2O . .	3·45	1·66	1·28	1·07	0·92	0
Solids	$Rb_2Cr_3O_{10}$		$Rb_2Cr_4O_{13}$		CrO_3	

The results are plotted in Fig. 46; where the solubility curve *ab* refers to the solid phase CrO_3; *bc*, to $Rb_2Cr_4O_{13}$; *cd*, to $Rb_2Cr_3O_{10}$; *de*, to $Rb_2Cr_2O_7$; *ef*, to Rb_2CrO_4; and *fg*, to $RbOH.nH_2O$.

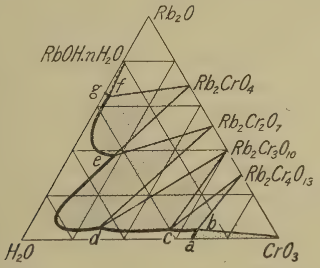


FIG. 46.—Equilibrium Diagram for the Ternary System: Rb_2O–CrO_3–H_2O.

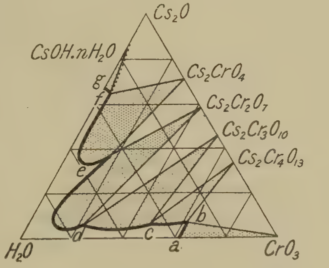


FIG. 47.—Equilibrium Diagram for the Ternary System: Cs_2O–CrO_3–H_2O at 30°.

C. Chabrié[6] obtained **cæsium chromate,** Cs_2CrO_4, by treating silver chromate with a boiling soln. of cæsium chloride, and evaporating the filtrate for crystallization; or more simply from an aq. soln. of chromic acid and cæsium carbonate. According to F. R. Fraprie, the crystals exist in two forms. C. Chabrié's process furnishes the so-called α-crystals in pale yellow, trigonal prisms with the axial ratio $a : c = 1 : 1{\cdot}2314$; while the β-crystals form dark yellow, rhombic bipyramidal crystals with the axial ratios $a : b : c = 0{\cdot}5640 : 1 : 0{\cdot}7577$, and which show twinning about the (130)-plane. These crystals are completely isomorphous with the potassium chromate family—a subject also discussed by J. W. Retgers. T. V. Barker studied parallel overgrowths on alkali sulphates and chromates. F. A. H. Schreinemakers and D. J. Meijeringh observed that in the ternary system: Cs_2O–CrO_3–H_2O at 30°, the composition of the soln. expressed in percentages, is:

CrO_3 .	0	0·119	9·662	13·08	8·98	2·16	4·57
Cs_2O .	70·63	69·22	31·68	35·08	24·05	3·04	1·61
Solids.	$CsOH.nH_2O$		Cs_2CrO_4		$Cs_2Cr_2O_7$		

CrO_3 .	4·57	25·59	44·45	55·17	62·70	62·50	62·28
Cs_2O .	1·61	0·096	3·13	3·90	4·35	2·33	0
Solids.		$Cs_2Cr_3O_{10}$		$Cs_2Cr_4O_{13}$		CrO_3	

The line *ab*, Fig. 47, is the solubility curve with CrO_3 as solid phase; *bc*, with $Cs_2Cr_4O_{13}$; *cd*, with $Cs_2Cr_3O_{10}$; *de*, with $Cs_2Cr_2O_7$; *ef*, with Cs_2CrO_4; and *fg*, with $CsOH.nH_2O$. The sodium and ammonium salts are alone hydrated in the ternary systems at 30° and the solubilities of the different alkali chromates at 30° are:

	Li	Na	NH_4	K	Rb	Cs
M_2CrO_4 .	49·98	46·63	28·80	39·63	44·14	47·0

M. Rosenfeld[7] obtained a green precipitate on adding a soln. of cuprous chloride in a conc. soln. of sodium chloride to an excess of a soln. of potassium chromate. The reaction was studied by H. J. P. Venn and V. Edge. Complex precipitates are formed differing in colour and constitution according to the method of preparation. The reaction consists essentially in the oxidation of the cuprous salt, and the formation of basic compounds whose composition changes when they are washed. The ultimate reactions are represented by: $3Cu_2Cl_2+2K_2CrO_4+8H_2O=4KCl+CuCl_2+5Cu(OH)_2+2Cr(OH)_3$, and $3Cu_2Cl_2+K_2Cr_2O_7+7H_2O=2KCl+2CuCl_2+4Cu(OH)_2+2Cr(OH)_3$. Intermediate products are represented by $2CuO.CuCl_2.3H_2O$, and $3CuO.CuCl_2.4H_2O$. J. Schulze reported normal **copper chromate,** $CuCrO_4$, to be formed when copper hydroxide is heated with an excess of a soln. of potassium dichromate in a sealed tube at 220°. Under ordinary conditions, J. Schulze, and M. Prud'homme and F. Binder found that a boiling soln. of the dichromate and copper hydroxide forms a basic chromate. According to G. Brügelmann, and J. C. G. de Marignac, the spontaneous evaporation of an aq. mixture of sat. soln. of copper sulphate and potassium dichromate gives first a crop of crystals of potassium sulphate, and then mixed crystals of chromates of indefinite composition. G. Quincke studied the formation of copper chromate by the diffusion of a soln. of copper sulphate into gelatine containing sodium dichromate. S. H. C. Briggs obtained normal copper chromate from a soln. of 3 grms. of copper carbonate with 6·9 per cent. CuO in 2·4 grms. of chromium trioxide dissolved in 20 c.c. of water, and, when the evolution of carbon dioxide has ceased, heated in a sealed tube for 2 or 3 hrs. at 200°; and also by boiling, in a vessel fitted with a reflux condenser, a mixture of 12 grms. copper carbonate, 21 grms. chromium trioxide, and 15 c.c. of water over an oil-bath; the product was washed with water and dried in a desiccator. H. Kopp, and G. C. Gmelin obtained crystals of copper chromate, isomorphous with pentahydrated copper sulphate, from a soln. of copper hydroxide in aq. chromic acid. M. Prud'homme said that if a soln. of chromic and cupric oxides in alkali-lye be allowed to stand some months, it deposits crystals of cupric chromate. H. W. Morse studied the rhythmic precipitation of the chromate.

J. Schulze said that the crystals are iron-black or reddish-brown with the appearance of hæmatite; the salt forms copper chromite at 400°. L. and P. Wöhler found that decomposition begins at 325°; at 340°, the partial press. of the oxygen is 417 mm.; and at 380°, over 750 mm. No state of equilibrium was observed. At 650°, cuprous chromite is formed. J. Schulze said that cupric chromate is insoluble in water, but it is soluble in acids including chromic acid. The salt is hydrolyzed by boiling water, leaving a basic chromate—possibly $3CuO.CrO_3.2H_2O$—as a residue. S. H. C. Briggs said that cupric chromate is not soluble in a soln. of copper sulphate.

According to M. C. Schuyten, when an aq. soln. of copper sulphate and potassium dichromate is treated with ammonia, or if potassium dichromate be added to an ammoniacal soln. of cupric hydroxide from which the excess of ammonia has been removed by exposure to air, **copper tetratotriamminochromate,** $4CuCrO_4.3NH_3.5H_2O$, separates as a brown, amorphous powder; when heated, it evolves ammonia, water, and a small quantity of nitrous fumes, but the whole of the ammonia and water cannot be expelled even by heating for a long time at a high temp. It dissolves in hydrochloric acid or ammonia, forming a yellow or a green soln. respectively; it is also easily soluble in a soln. of silver nitrate, but insoluble in organic solvents. Alcohol is not oxidized to aldehyde by boiling with the hydrochloric acid soln. of this compound. S. H. C. Briggs obtained **copper hemiheptamminochromate,** $2CuCrO_4.7NH_3.H_2O$, by pouring an aq. soln. of 14 grms. of copper carbonate and 25 grms. of chromium trioxide into a mixture of 125 c.c. conc. aq. ammonia, 50 c.c. of water, and 15 grms. of potassium hydroxide and allowing it to stand exposed to air. The greenish-black crystals lose ammonia at ordinary temp.; they are decomposed by water; and are soluble in dil. aq. ammonia. N. Parravano and A. Pasta prepared **copper tetramminochromate,** $CuCrO_4.4NH_3$, by adding alcohol to a soln. of copper tetrapyradinochloride in aq. ammonia; the green prismatic crystals are decomposed by water.

L. N. Vauquelin said that when potassium "chromate" is added to a soln. of a neutral copper salt, a chestnut-brown precipitate is produced, which, according C. Gerhardt, and C. Freese, consists of $K_2O.3CuO.3CrO_3.2H_2O$, or, according to M. Gröger, $KCu_2(OH)(CrO_4)_2.H_2O$, and which, according to G. C. Gmelin, furnishes potassium dichromate when treated with boiling water. A. Bensch noticed that when potassium chromate is added to a boiling, aq. soln. of copper sulphate, the blue colour changes from green to yellow to red, and then a brown precipitate forms. B. Skormin obtained **copper trioxychromate,** $3CuO.CuCrO_4.3H_2O$, by the action of an alkaline soln. of an excess of potassium chromate on a soln. of copper sulphate. F. J. Malaguti and M. Sarzeau said that after repeated extraction with boiling water, there remains—according to the analyses of F. J. Malaguti and M. Sarzeau, J. Persoz, C. Freese, J. Schulze, L. Balbiano, M. Gröger, and M. Rosenfeld—**copper dioxychromate,** $3CuO.CrO_3.2H_2O$, or $2Cu(OH)_2.CuCrO_4$; and, added M. Gröger, the same product is obtained whether the potassium chromate or the copper salt be in excess. This salt was also prepared by B. Skormin. According to M. Rosenfeld, this compound is formed when potassium chromate is added to a soln. of copper sulphate; although the colour of the substance varies with the temp. and conc. of the soln. its composition is constant. The same salt is formed by digesting freshly precipitated copper hydroxide with a soln. of potassium dichromate, but in this case it is mixed with crystals of potassium dichromate. M. Gröger said that the amorphous rust-brown precipitate, obtained by mixing aq. soln. of copper sulphate and potassium chromate, becomes crystalline when left in contact with excess of the copper salt soln. The precipitate is basic potassium cupric sulphatochromate, the proportion of sulphate present depending on the conc. of the copper salt soln. and the duration of its contact with the precipitate. The double salt is rapidly decomposed either by boiling water or by fusion, but without forming potassium chromate. The same precipitate is obtained on adding potassium hydroxide to the mixture of cupric sulphate and potassium dichromate in aq. soln. as indicated by A. Knopp. M. Gröger also said that the addition of sodium chromate to an aq. soln. of copper chloride results in the formation of a greenish-yellow precipitate which, when left in the mother-liquor, gradually assumes a bright rusty-brown colour, but does not become crystalline. The greenish-yellow substance is the basic cupric chromate, $2Cu(OH)_2,CuCrO_4$; the rusty-brown precipitate contains a larger proportion of chromic acid, which is removed by washing with water, the greenish-yellow salt being regenerated. According to L. Balbiano, a soln. of cupric sulphate is not completely precipitated by neutral ammonium chromate, the complete precipitation only being effected by the addition of ammonia.

Both the precipitate first produced by the ammonium chromate and that by the later addition of the ammonia have the same composition, $2CuO.CuCrO_4.2H_2O$. If the aq. soln. be evaporated on the water-bath, an amorphous mass is formed. Alcohol precipitates from the aq. soln. a dirty green precipitate, and is at the same time oxidized to acetic acid. In repeating L. Balbiano's experiments, M. Gröger observed that the original precipitate contains ammonium, and this salt furnishes the basic salt, $2Cu(OH)_2.CuCrO_4$, by washing with boiling water. A. Viefhaus obtained the same basic salt by digesting barium chromate with an aq. soln. of copper sulphate for 3 days at 30° to 35°; C. Freese, and M. Rosenfeld, by treating copper oxide or hydroxide with a boiling soln. of potassium dichromate, and extracting the product with boiling water; C. Freese, and R. Böttger, similarly treated copper carbonate with an aq. soln. of chromic acid. J. Schulze obtained this basic salt by the action of boiling water on copper chromate; and F. Dröge, by the action of boiling water on copper decamminodioxychromate. The dark brown flocculent precipitate dries at 100° to a dark brown, almost black, amorphous powder. J. Persoz said that it loses no water at 170°, but decomposes at a red-heat. F. J. Malaguti and M. Sarzeau said that it is soluble in dil. nitric acid, and in aq. ammonia. G. Gore observed that it is insoluble in liquid ammonia; R. Böttger, that it is decomposed by alkali-lye forming copper oxide; J. W. Slater, that when boiled with phosphorus, it forms copper, copper phosphide and phosphate, chromic phosphate, and phosphorus and phosphoric acids. R. Otto recommended its use in the determination of sulphur in organic analyses.

According to H. Moser, potassium dichromate does not give a precipitate with an aq. soln. of a copper salt; but, added W. E. Garrigues, if an excess of ammonia or, according to A. Kopp, and M. Rosenfeld, if sufficient potassium hydroxide be present to transform the dichromate into monochromate, a precipitate is formed which may be reddish-brown, greenish-yellow, green, or blue according to the proportion of alkali employed—the blue precipitate is copper hydroxide.

M. Rosenfeld supposed that the yellow precipitate just indicated is a basic salt *copper pentoxybischromate*, $7CuO.2CrO_3.5H_2O$; and the green precipitate, which changes to brown on drying, basic *copper hexoxychromate*, $7CuO.CrO_3.5H_2O$—probably both basic salts are mixtures of copper hydroxide and the dioxychromate. The green-coloured substance prepared by C. W. Juch by the action of 2 parts of potassium carbonate and one part of calcium carbonate on a soln. of 48 parts of copper sulphate and 2 parts of potassium dichromate; and that obtained by T. Leykauf by the action of ammonia on a soln. of 2 parts of copper sulphate and one part of potassium dichromate are also mixtures.

According to M. Vuaflart, if copper chromate be treated with aq. ammonia, the dark green soln. does not decolorize on exposure to light, and if evaporated, or cautiously treated with acids, the original chromate is restored. R. Böttger added that if the green soln. be covered with alcohol, it deposits a dark green powder, which, after washing with alcohol, furnishes, according to the analysis of F. J. Malaguti and M. Sarzeau, **copper decamminomonoxybischromate,** $CuO.2CuCrO_4.10NH_3.2H_2O$. The salt was also prepared by A. Kopp. The powder consists of dark green, acicular crystals, which lose ammonia in air; and when heated decompose with a feeble detonation. The salt is decomposed by water. According to P. A. Bolley, F. Dröge, W. Grüne, J. Stinde, and I. C. Zimmermann, the green soln. was formerly used in dyeing.

M. Gröger could not isolate **ammonium copper chromate** of definite composition; the precipitate obtained by treating copper chloride with ammonium chromate, is readily transformed into copper oxychromate. S. H. C. Briggs, and M. Gröger obtained **ammonium copper diamminochromate,** $(NH_4)_2CrO_4.CuCrO_4.2NH_3$, by the action of cupric chloride on a soln. of ammonium chromate containing an excess of ammonia; or of a soln. of copper carbonate in chromic acid on conc. aq. ammonia. The dark green crystals lose water and ammonia at 200°. The salt is hydrolyzed by water. M. Gröger mixed 2 vols. of a soln. of 85·3 grms. of $CuCl_2.2H_2O$ in a litre of water with one vol. of a soln. of 97·2 grms. of potassium chromate in a litre of water. After standing 4 days, at room temp., the precipitate was washed with cold water by suction, and dried at 100°. The brownish-red powder consists of microscopic, four-sided, prismatic crystals of **potassium copper oxyquadrichromate,** $K_2O.4CuO.4CrO_3.3H_2O$, or $K(OH)Cu_2(CrO_4)_2.H_2O$. It is rapidly decomposed by boiling water. A. Knop reported **potassium copper oxytrischromate,** $K_2O.3CuO.3CrO_3.2H_2O$, to be formed by the action of a soln. of potassium dichromate on freshly precipitated copper hydroxide, or by gradually adding a soln. of potassium hydroxide to a mixed soln. of copper sulphate and potassium dichromate. The salt was also prepared by B. Skormin. M. Rosenfeld supposed that this product is impure copper dioxychromate, and M. Gröger, impure potassium copper oxyquadrichromate. C. Gerhardt, and C. Freese supposed the precipitate produced by potassium chromate in a cold soln. of copper sulphate to be potassium copper oxytrischromate. The pale brown powder consists of microscopic, six-sided plates. The salt loses water when heated. Boiling water extracts potassium dichromate. The salt is soluble in a soln. of ammonia and ammonium carbonate. F. Rose, S. Tschelnitz, J. G. Gentele, and G. Zerr and G. Rübencamp mentioned the use of the basic chromate as a reddish-brown pigment under the name *chrome brown.*

According to S. H. C. Briggs, **potassium copper diamminochromate,** $K_2CrO_4.CuCrO_4.2NH_3$, crystallizes out when an ammoniacal soln. of copper chromate to which a large proportion of potassium chromate has been added, is allowed to lose its free ammonia by exposure to air. The crystals were washed by decantation with the mother-liquid, then with dil. ammonia, and finally with alcohol and ether. It is slowly decomposed at 250°, rapidly at 280°; it is decomposed by water; and is soluble in aq. ammonia. M. Prud'homme added a cupric salt to a mixture of sodium hydroxide and chromate, and obtained a yellowish-green soln. of **sodium copper chromate.** A similar soln. is produced by boiling an excess of copper oxide with a soln. of chromic oxide in soda-lye.

According to F. Wöhler and F. Rautenberg,[8] silver chromate can be reduced to *silver subchromate,* possibly Ag_4CrO_4, at ordinary temp. The black powder always contains some metal; the reduction to silver is completed at 50°. The subchromate is coloured red by nitric acid and then dissolved; and with dil. acids a green soln. is formed. W. Muthmann showed that the alleged subchromate is a mixture of ordinary silver chromate and silver.

L. N. Vauquelin [9] obtained **silver chromate,** Ag_2CrO_4, by dropping a dil. soln. of potassium chromate into a conc. soln. of silver nitrate, and washing the dark reddish-brown precipitate—if the silver nitrate soln. be dropped into the chromate soln., the precipitate is orange-red, and is contaminated with the potassium salt, which is very difficult to remove by washing. N. W. Fischer found that silver oxide abstracts chromic acid from a soln. of potassium chromate leaving the liquid alkaline, but a large excess of the oxide does not remove all the chromic acid except when added in the form of its ammoniacal soln. J. Milbauer obtained a 10 per cent. conversion to chromate when a mixture of silver carbonate or oxide and chromic oxide is heated to 480° in oxygen at 12 atm. press. C. Freese obtained silver chromate by boiling silver oxide for some days with a soln. of potassium chromate or dichromate. I. Guareschi obtained silver chromate by the action of a conc. soln. of chromic acid on silver bromide; and M. Gröger, by the action of water on ammonium silver chromate. R. Warington found that when silver dichromate is boiled with water it forms silver chromate; according to E. Jäger and G. Krüss, and B. M. Margosches, the boiling should be continued as long as anything passes into soln. R. Warington also found that when an ammoniacal soln. of silver dichromate is evaporated spontaneously, a greenish crust of the monochromate is formed. F. A. Gooch and R. S. Bosworth showed that silver is precipitated quantitatively as chromate by adding an excess of potassium chromate to a soln. of silver nitrate. The chromate can be purified by dissolving it in aq. ammonia, and reprecipitating it by boiling the soln. G. P. Baxter and co-workers described the preparation of the salt, and added that it can be dried by heating it for 2 hrs. at 225° in a current of dry air. According to A. Lottermoser, by adding $\frac{1}{40}N$-$AgNO_3$

to an excess of $\frac{1}{40}N$-CrO_3, **colloidal silver chromate** is produced; the hydrosol soon becomes turbid. The Chemische Fabrik von Heyden reported that if silver chromate be formed in the presence of proteins as protective colloid, and the soln. dialyzed, or precipitated by the addition of an acid, and afterwards peptized by dil. alkali-lye, the hydrosol is stable. N. R. Dhar and A. C. Chatterji found silver chromate is not peptized by conc. soln. of cane-sugar; and N. R. Dhar and S. Ghosh that it is peptized by ammonium nitrate. N. R. Dhar and A. C. Chatterji studied the adsorption of silver ions by silver chromate. According to F. Köhler, when silver nitrate and ammonium dichromate react as a result of the diffusion which takes place when an aq. soln. of the one salt is placed in contact with a gelatinized soln. of the other, precipitation rings are formed which exhibit rhythmic character. When the ammonium salt is contained in the gelatin layer the ring formation varies with the conc. of the dichromate. At low concentrations, the rings are only partly developed, and at high concentrations they are blurred, but over an intermediate range the ring system is well developed. If the gelatin layer contains the silver salt, similar results are obtained, except that no rings are formed when the conc. is small. The conc. of the gelatin also affects the ring formation in the sense that with increasing conc. the rings become less well defined. It seems probable that rhythmic precipitation phenomena in gelatin-water systems are dependent on the existence of a more or less definite relation between the velocities of diffusion of the reacting substances and the velocity of crystallization of the products of the reaction. In the rhythmical precipitation of silver chromate by means of ammonium dichromate the small crystals of ammonium nitrate which also separate rhythmically are coloured by silver chromate, being yellowish-green to red, according to the conc. Similar coloured crystals are obtained when a soln. of ammonium nitrate containing a little ammonium dichromate is mixed with a drop of silver nitrate and allowed to evaporate on a glass slide. Exactly similar crystals are obtained when potassium dichromate is used. N. R. Dhar and co-workers supposed that the rings are produced by the coagulation of peptized silver chromate. The subject was studied by H. Bechold, H. N. Holmes, E. Hatschek, R. E. Liesegang, N. R. Dhar and A. C. Chatterji, K. C. Sen and N. R. Dhar, A. M. W. Williams and M. R. MacKenzie, T. R. Bolam and M. R. Mackenzie, G. Linck, B. Kisch, M. S. Dunin and F. M. Schemjakin, E. C. H. Davies, A. Janek, A. Steopoe, M. Storz, C. K. Jablcznysky and A. Klein, C. K. Jablczynsky, F. G. Toyhorn and S. C. Blacktin, P. B. Ganguly, R. Fricke, W. Ostwald, F. Köhler, H. McGuigan, E. R. Riegel and M. C. Reinhard, T. R. Bolam and B. N. Desal, S. S. Bhatnagar and J. L. Sehgal, L. N. Mukherjee and A. C. Chatterji, F. M. Shemjakin, H. Westerhoff, F. Pannach, H. W. Morse, W. W. Siebert, D. N. Ghosh, and S. Hedges and R. V. Henley.

Silver chromate varies in colour according to the mode of preparation, and it is described as forming tabular or acicular crystals or a dark green or purple-red crystalline powder. R. Hunt thought that the variations in colour depended on the exposure of the potassium dichromate soln. to light, for he said that the chromate produced by the actinized soln. has a "much more beautiful colour" than when produced by a soln. of dichromate which had not been exposed to light. F. Bush showed that there is no difference in the colour of silver chromate derived from insolated and non-insolated soln. of potassium dichromate, but that the rate of the mixing of the soln. determines the difference in the colour and the physical characteristics of the resulting silver chromate. C. Freese, W. Autenrieth, and B. M. Margosches found that the red variety is produced by precipitation from a silver salt with a chromate or dichromate if the silver is in excess. The result is not affected by temp. On the other hand, when silver dichromate is decomposed by cold or hot water, or when a soln. of silver chromate or dichromate is evaporated, R. Warington, E. Jäger and G. Krüss, W. Autenrieth, and B. M. Margosches observed that green crystals are produced. It has therefore been suggested that silver chromate exists in two forms: (i) red—varying from orange to deep reddish-brown; and (ii) green—varying from dark green to greenish-black, but red in transmitted light, or in the powdered form. It has not been proved whether this is a case of polymorphism, or whether the effect is produced by the varying sizes of the crystalline granules. F. Köhler said that both silver chromate and dichromate can take small quantities of ammonium or potassium nitrate into solid soln. The colour of pure silver chromate is always greenish-black, and the red substance supposed to be a separate modification is really a mixture of silver chromate and a solid soln. of that salt with nitrates. M. Copisarow observed that tree-like, dendritic forms are produced when the precipitate is slowly formed. According to J. W. Retgers, and W. Autenrieth, the red crystals are rhombic with a pleochroism—pale reddish-brown, and brownish-black—they are not isomorphous with silver sulphate but may be so with sodium sulphate.

H. G. F. Schröder gave 5·536 for the sp. gr. of green silver chromate, and 5·523 for that of the red variety; and G. P. Baxter and co-workers gave 5·625 at 25°/4°, for the red crystals; M. L. Dundon, 5·52, and the mol. vol. 60·1 at 26°. M. L. Dundon gave 2 for the hardness, and 575 ergs per sq. cm. for the surface energy at the interface of the solid and water at 26°. According to L. N. Vauquelin, silver chromate melts in the oxidizing flame of the blowpipe; and in the inner flame, it is reduced to silver and chromic oxide. F. Kohlrausch gave for the sp. electrical conductivity of sat. soln. of silver chromate:

	0·26°	14·82°	18°	30·76°	37·30°	75°
Conductivity .	$0{\cdot}0_5667$	$0{\cdot}0_41561$	$0{\cdot}0_4186$	$0{\cdot}0_4350$	$0{\cdot}0_4460$	$(0{\cdot}0_3160)$ mho.

T. R. Bolam and M. R. MacKenzie found the sp. conductivity of soln. of silver chromate and gelatine to be:

Ag_2CrO_4 .	0·00333*N*-	0·00250*N*-	0·00125*N*-	0·00236*N*-	0·00118*N*-	0·00162*N*-
Mho $\times 10^{-3}$.	0·8341	0·6841	0·4636	0·5916	1·3703	0·4207
Gelatine .	3	3	3	1·59	1·59	0·07 per cent.

The conductivities are slightly smaller when the gelatine is set than when it is liquid. The electromotive force of cells with Ag | $0{\cdot}1N$-$AgNO_3$, $10N$-NH_4NO_3, x | Ag, is 0·1483 volt when x is a sat. soln. of Ag_2CrO_4; 0·1469 volt with the same soln. with $0{\cdot}01NaNO_3$; and 0·2247 volt with the salt. soln. of silver chromate plus $0{\cdot}1N$-K_2CrO_4.

For the reducing action of hydrogen, *vide supra.* Silver chromate is very sparingly soluble in ammonia. Expressing the solubilities, S, in milligrams of silver chromate per 100 grms. of water, F. Kohlrausch gave $S=2{\cdot}52$ at 18°, from the electrical conductivity; G. S. Whitby, $S=2{\cdot}56$ at 18°, from colorimetric observations; R. Abegg and A. J. Cox, $S=2{\cdot}0$ at 25°, from potential measurements; R. Abegg and H. Schäfer, $S=2{\cdot}9$ at 25°, from the equilibrium of silver chromate and dichromate; M. S. Sherrill, $S=4{\cdot}1$ at 25°, from the solubility of silver chromate in ammonia; G. S. Whitby, $S=3{\cdot}41$ at 27°, from colorimetric observations; O. Hähnel, $S=5{\cdot}4$ at 35°, from the equilibrium with silver iodate and chromate; G. S. Whitby, $S=5{\cdot}34$ at 50°, from colorimetric observations; and R. F. Carpenter obtained $S=4{\cdot}1$ at 100°. Other observations were made by L. L. de Koninck and E. Nihoul, G. Meinecke, W. G. Young, and R. F. Carpenter. R. Abegg and H. Schäfer obtained for the solubility product $[Ag^{\cdot}]^2[CrO_4']=2{\cdot}64\times10^{-12}$ at 25°, from the equilibrium between silver chromate and dichromate. M. S. Sherrill calculated 9×10^{-12} at 25°, from the solubility of silver chromate in ammonia; and O. Hähnel, $17{\cdot}7\times10^{-12}$ at 35°, from the equilibrium in the reaction $2AgIO_3'+CrO_4'' \rightleftharpoons Ag_2CrO_4+2IO_3'$. B. M. Margosches found that the solubility is diminished by the presence of $Ag^{\cdot}$-ions, or CrO_4''-ions, but in a conc. soln. of potassium chromate the solubility is increased. The solubility in acids is dependent on the grain-size and of the presence of silver chromate. M. L. Dundon observed a 10 per cent. increase in the solubility when the particles are reduced to $0{\cdot}3\mu$ diameter. J. Krutwig found that chlorine liberates oxygen from silver chromate at 200°, forming silver chloride and small red crystals of chromium trioxide. The relatively great solubility of silver chromate with respect to the chloride explains its use as an indicator in the titration of chlorides by a silver salt; so long as an appreciable amount of chloride is present, silver chromate is converted into chloride, but as soon as the chloride is all consumed, the dark red colour of silver chromate appears. According to A. A. Hayes, silver chromate is decomposed by hydrochloric acid and soluble chlorides, and L. L. de Koninck and E. Nihoul said that the decomposition of the chromate by chlorides, bromides, and iodides is quantitative. B. M. Margosches found that the reaction with the alkali halides is fast only with freshly precipitated silver chromate. E. Ramann and H. Sallinger studied the system: $K_2CrO_4 + AgIO_3 \rightleftharpoons KIO_3 + Ag_2CrO_4$. W. R. Hodgkinson and J. Young studied the reduction of the salt by dry sulphur dioxide. A. A. Hayes found that the chromate is decomposed by soln. of sulphates. E. C. Franklin and C. A. Kraus said that silver chromate is insoluble in liquid ammonia. The chromate is slowly dissolved by cold, dil., aq. ammonia, and rapidly by hot, conc., aq. ammonia. The solubility of the chromate in aq. ammonia was measured by M. S. Sherrill, and the results expressed in S mols per litre:

NH_4OH	0·01	0·02	0·04	0·08
S	2·04	4·169	8·595	17·58

The increased solubility with ammonia is attributed to the formation of the soluble complex $Ag(NH_3)_2CrO_4$. E. Mitscherlich, G. Meinecke, and B. M. Margosches obtained from the soln. in conc. aqua ammonia yellow tetragonal crystals of **silver tetramminochromate,** $Ag_2CrO_4.4NH_3$, with the axial ratio $a:c=1:0{\cdot}5478$. H. Topsöe gave 2·717 for the sp. gr. M. S. Sherrill's results are as follows:

HNO_3	0·01	0·02	0·04	0·075
$[Ag^{\cdot}]\times 10^3$	5·808	7·488	10·02	12·41
$[HCrO_4']\times 10^3$	2·245	2·775	3·530	4·220
$[Cr_2O_7']\times 10^3$	0·3775	0·577	0·935	1·333

The tetramminochromate in air loses ammonia more rapidly than the selenate, and potash-lye precipitates fulminating silver from the aq. soln.

B. M. Margosches found that the solubility of silver chromate in nitric acid depends on the age of the salt. L. L. de Koninck and E. Nihoul measured the solubility of the chromate in nitric acid; and R. F. Carpenter, the solubility in soln. of the nitrates. M. S. Sherrill and D. E. Russ said that soln. containing more than 0·075N-HNO_3 form silver dichromate; while F. A. Gooch and R. S. Bosworth said that the chromate is insoluble in dil. nitric acid in the presence of enough potassium chromate to form with the nitric acid, dichromate and nitrate; silver chromate is also said to be insoluble in a soln. of sodium nitrate. F. A. Gooch and L. H. Weed also found the chromate insoluble in a soln. of silver nitrate; aq. soln. containing 3·24 grms. of the salt named per 100 c.c. were found to dissolve at 100° the following amounts:

	Water	$NaNO_3$	KNO_3	NH_4NO_3	$MgNO_3$
Ag_2CrO_4	0·00415	0·00415	0·0124	0·0207	0·0166

B. M. Margosches said that silver chromate is practically insoluble in a soln. of silver nitrate, whilst sodium phosphate soln. form silver phosphate. Silver chromate is practically insoluble in conc. acetic acid, but some is dissolved by dil. acetic acid. A soln. of potassium chromate also dissolves a little silver chromate. A. Jaques studied the reaction with ethyl bromide. B. Guerini found that 11·65 per cent. alcohol dissolves 0·0129 grm. of silver chromate at ordinary temp. According to L. N. Vauquelin, several metals immersed in water and in contact with silver chromate exert a reducing action; and N. W. Fischer said that cadmium separates silver; zinc separates brownish-black, arborescent silver; tin, lead, and iron, a brown spongy mass; arsenic, a brown powder; copper, and mercury have a feeble action; and antimony, none. The precipitates may be contaminated with green chromic oxide; and the liquid may acquire a yellow tinge from the presence of chromic acid. With an ammoniacal soln. of silver chromate, zinc is said to precipitate silver and chromium; cadmium, silver; copper, a grey powder; lead, silver; while tin, iron, and antimony give no precipitation. C. Freese observed that a soln.

of potassium hydroxide extracts all the chromic acid from silver chromate. J. F. G. Hicks and W. A. Craig found that silver chromate undergoes a reaction with an equimolar mixture of fused potassium and sodium nitrates at about 240°, forming basic chromate analogous to a hydrolytic reaction. A state of equilibrium is established; but with fused sodium chloride, at about 870°, the reaction is complete. P. Ray and J. Dasgupta prepared a complex with hexamethylenetetramine. S. J. Thugutt found that aragonite is coloured red whilst calcite is not changed when the minerals are treated with 0·1*N*-$AgNO_3$, and afterwards wetted with a 20 per cent. soln. of potassium dichromate.

M. Gröger obtained a precipitate by the action of an almost sat. soln. of potassium chromate on silver nitrate. The precipitate contained potassium and silver chromates, but he could not decide whether these were mechanically mixed or combined as *potassium silver chromate.* M. Gröger prepared **ammonium silver chromate,** $(NH_4)_2CrO_4.3Ag_2CrO_4$, by dropping a conc. soln. of silver nitrate into a cold, sat. soln. in ammonium chromate, and allowing the mixture to stand for some weeks; he also obtained the same salt by the action of silver nitrate on an ammoniacal soln. of ammonium chromate. The garnet-red powder or hexagonal crystals are decomposed by heat, and by water.

N. A. Orloff [10] prepared an orange-coloured soln. of **gold chromate,** $Au_2(CrO_4)_3$, by adding a soln. of auric chloride to an excess of freshly precipitated silver chromate, and filtering off the silver chloride. If the conc. soln. be evaporated in a desiccator, crystals with the composition $Au_2(CrO_4)_3.CrO_3$ are formed.

In the extraction of chromium by the calcination of a mixture of chromite and limestone, **calcium chromate,** $CaCrO_4$, is formed as an intermediate product—*vide supra.* J. Milbauer observed a 56·9 per cent. conversion to chromate when a mixture of chromic oxide and calcium oxide or carbonate is heated to 480° in oxygen at 12 atm. press. M. R. Nayer [11] and co-workers found that calcium and chromic oxides begin to interact in the presence of air to form calcium chromate at 650°; at 700°, a 95 per cent. yield of chromate is obtained with mixtures containing 2 equivalents of calcium oxide to 1 of chromic oxide and a 60 per cent. yield when the ratio is 1 : 1. In the presence of excess of calcium oxide, equilibrium is attained at about 800°, although pure calcium chromate does not begin to decompose until 1000° is reached. A mixture of calcium oxide, sodium carbonate, and chromium trioxide (1·7 : 0·65 : 1) gave a quantitative yield of chromate in 4 hrs. at 660° and in 5 minutes at 1050°. K. Herrmann and co-workers found that the crystals are rhombic bipyramids and that the crystal unit contains 4 mols, and has a=7·45 A., b=10·3 A., and c=5·85 A. When calcium chromate is decomposed by heat no basic salts are formed. As shown by T. Thomson, and H. Moser, a soln. of calcium chloride slowly forms a precipitate when treated with potassium dichromate; as shown by J. F. Bahr, the precipitate varies in composition, according to the conditions, from $CaCrO_4$ to $5CaCrO_4.K_2CrO_4$. If free acetic acid be present, H. Kämmerer, and F. T. Frerichs observed no precipitation; and F. Kuhlmann found that calcium carbonate is only partially converted into the chromate by a soln. of potassium chromate; lime-water gives no precipitate with a soln. of potassium chromate. F. Mylius and J. von Wrochem obtained the anhydrous chromate by heating the hydrated salt—G. N. Wyrouboff said at 300°—or by warming a supersaturated soln., containing 15 to 20 per cent. $CaCrO_4$, over 36°. The yellow powder consists of fine needles. L. Bourgeois obtained crystals of the anhydrous chromate by melting a mixture of 2 eq. of calcium chloride with an eq. each of potassium and sodium chromates. D. Vorländer and H. Hempel observed no transformation into

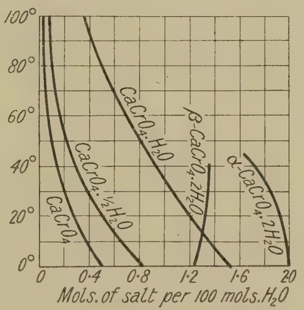


Fig. 48. — The Solubility Curves of Calcium Chromate.

an isotropic form when the alkaline earth chromates are heated. The sat., aq. soln. at 18° has a sp. gr. 1·023 and contains 2·3 per cent. $CaCrO_4$. It is very stable, and is not hydrated by standing for a year in contact with water. Three hydrates have been reported. The percentage solubility, *S*, of stable $CaCrO_4$ is :

	0°	20°	30°	50°	70°	100°
S .	4·31	2·23	1·92	1·11	0·80	0·42

The results are plotted in Fig. 48. By mixing a 15 per cent. soln. of calcium chromate with calcium chloride or glycerol, and rapidly warming to 100°, small, doubly refracting, presumably rhombic crystals of the *hemihydrate*, $CaCrO_4.\frac{1}{2}H_2O$, are formed. They lose water at 400° ; and a soln., sat. at 18°, has 4·4 per cent. $CaCrO_4$, and a sp. gr. of 1·044. The percentage solubility, *S*, of the unstable hemihydrate, Fig. 48, is :

	0°	18°	30°	50°	70°	100°
S .	6·80	4·4	3·66	1·60	1·10	0·80

According to H. von Foullon, the *monohydrate*, $CaCrO_4.H_2O$, is produced when the mother-liquor from the dihydrate is evaporated over 25° ; and F. Mylius and J. von Wrochem obtained it by heating the rhombic β-dihydrate at 12°. The orange-red, rhombic, bipyramidal crystals were found by F. von Foullon to have the axial ratios $a : b : c = 0·6296 : 1 : 0·6404$. G. N. Wyrouboff gave 0·9917 : 1 : 0·7995 and said that the crystals are similar to those of anhydrite. The sp. gr. is 2·793 at 15°, and the mol. vol. 62·4. F. Mylius and J. von Wrochem said that the dark yellow, four-sided, doubly refracting pyramids do not effloresce very much at ordinary temp. The soln. sat. at 18° has a sp. gr. 1·096, and contains 9·6 per cent. of $CaCrO_4$. The percentage solubility, *S*, Fig. 48, of the unstable monohydrate, is

	18°	25°	40°	60°	75°	100°
S .	9·60	9·09	7·83	5·75	4·58	3·10

J. F. Bahr said that when calcium carbonate is treated with a soln. of chromic acid, the dihydrate, $CaCrO_4.2H_2O$, is formed ; and M. Siewert obtained the dihydrate by evaporating in vacuo a soln. of the carbonate in chromic acid. H. von Foullon said that the dihydrate exists in two forms. There is first the labile or *α-dihydrate* obtained by the slow evaporation below 25° of the mother-liquid from the basic salt, or up to 65° in the presence of sulphuric acid. F. Mylius and J. von Wrochem observed that it separates from a supersaturated soln. of calcium chromate at room temp. The sulphur-yellow, monoclinic crystals resemble those of the dihydrated calcium sulphate. There is the stable or β-dihydrate obtained by allowing the α-form to stand in contact with a sat. soln. of calcium chromate ; it also separates when the sat. soln. is allowed to stand for a week. H. von Foullon obtained crystals by evaporating a soln. at 22°. A. Fock also described the preparation of the dihydrate, and according to A. Fock, and H. von Foullon, the pale yellow, rhombic crystals do not resemble those of gypsum. The axial ratios are $a : b : c = 0·6942 : 1 : 0·7388$. The (100)-cleavage is complete. G. N. Wyrouboff could not prepare the dihydrate. M. Siewert said that the dihydrate loses its water when strongly heated, and every time it is heated it becomes cinnabar-red. F. Mylius and J. von Wrochem found that the β-dihydrate at 12° forms the monohydrate. At 18°, the sat. aq. soln. of the α-form contains 14·3 per cent. of $CaCrO_4$ and has a sp. gr. of 1·149 ; while with the β-form there is present 10·3 per cent. of $CaCrO_4$ and the sp. gr. is 1·105. M. Siewert, and H. Schwarz made observations on the solubility. F. Mylius and J. von Wrochem found that the percentage solubilities, *S*, Fig. 48, are :

	0°	20°	45°	0°	20°	40°
S .	14·70	14·20	12·40	9·83	10·20	10·40
	α-dihydrate			β-dihydrate		

The transition temp. for β-dihydrate⇌monohydrate is 10·20° with 14 per cent.

$CaCrO_4$. F. Kohlrausch measured the electrical conductivity of aq. soln. of the salt, while H. H. Hosford and H. C. Jones found for the mol. conductivity, μ mhos, between 0° and 35°, and S. F. Howard and H. C. Jones between 35° and 65°, the following values, when a mol of the salt is dissolved in v litres :

v	. .	8	16	32	128	512	1024	2048	4096
μ	0° .	62	69	77	97	114	119	—	124
	12·5° .	86	96	108	135	160	168	—	173
	25° .	113	126	142	179	212	223	—	230
	35° .	134	147	169	214	255	270	—	279
	65° .	200	229	260	337	412	428	288	—
α	0° .	49·70	85·64	62·19	78·55	91·90	96·12	98·54	100·00
	65° .	65·02	—	77·01	86·41	93·19	96·18	97·60	100·00

The percentage ionization, α, has also been calculated.

H. Caron and D. A. Raquet found dihydrated calcium chromate to be soluble in acids and in dil. alcohol. C. R. Fresenius found that 100 c.c. of 29 per cent. alcohol dissolve 1·216 grms. calcium chromate, and 100 c.c. of 53 per cent. alcohol, 0·88 grm. The anhydrous salt is insoluble in absolute alcohol ; and A. Naumann observed that it is insoluble in acetone. F. Guthrie observed that molten sodium nitrate dissolves 0·547 grm. of the salt. J. F. G. Hicks and W. A. Craig found that equimolar mixture of fused sodium and potassium nitrates, at about 870°, reacts with calcium chromate forming basic salts and entering into a state of equilibrium analogous to a hydrolytic reaction. L. Kahlenberg and W. J. Trautmann found that when calcium chromate is mixed with silicon and heated in the electric arc furnace there is a strong reaction, but in the bunsen burner there is a slight reaction. J. B. Hannay obtained *potassium calcium sulphatochromates*, $K_2CrO_4.CaSO_4,H_2O$; $2K_2CrO_4.CaSO_4$; and $K_2CrO_4.CaSO_4.Na_2SO_4.H_2O$. H. von Foullon obtained the basic salt, **calcium oxychromate,** $CaO.CaCrO_4.3H_2O$, by warming to 50°–60°, a soln. of calcium carbonate in a dil. aq. soln. of chromic acid ; or, according to F. Mylius and J. von Wrochem, from a soln. of chromic acid supersaturated with calcium hydroxide. The lemon-yellow, monoclinic prisms have the axial ratios $a:b:c=1·0311:1:0·6500$, and $\beta=98°\ 13'$. 100 parts of water dissolve 0·435 part of the salt.

K. S. Nargund and H. E. Watson found that when calcium chromate is heated to 1030° at less than 20 mm. press., **calcium dichromitochromate,** $3CaO.Cr_2O_3.CrO_3$, is formed ; if the press. be 2 mm., **calcium hexachromito*bis*chromate,** $8CaO.3Cr_2O_3.2CrO_3$, is produced ; and at lower press., **calcium tetrachromitochromate,** $5CaO.2Cr_2O_3.CrO_3$, results, and it has no measurable dissociation press. at 1030°. If calcium chromate mixed with lime is heated, **calcium oxy*bis*chromate,** $CaO.2CaCrO_4$, is formed, and it readily decomposes, forming **calcium dichromito*sexies*chromate,** $12CaO.Cr_2O_3.6CrO_3$, with a dissociation press. of 270 mm. at 910° ; and it decomposes, forming **calcium dichromito*quater*chromate,** $9CaO.Cr_2O_3.4CrO_3$, with a dissociation press. of 22 mm. at 920°. This product is also formed when a mixture of calcium oxide and chromate is heated in air ; the black compound is soluble in dil. acids, and when heated to 1030° furnishes **calcium dichromito*tris*chromate,** $6CaO.Cr_2O_3.3CrO_3$. A mixture of calcium chromate and chromic oxide yields **calcium dichromito*bis*chromate,** $2CaO.Cr_2O_3.2CrO_3$, with a dissociation press. of 150 mm. at 1030°, and finally a chromite.

A. Duncan found that a soln. of freshly burnt lime in an aq. soln. of potassium dichromate, when evaporated, gives orange-yellow crystals of **potassium calcium chromate,** $K_2CrO_4.CaCrO_4$, which are the *monohydrate* if the crystallizing soln. is boiling, and the *dihydrate*, if the soln. is at 80°. E. Schweizer obtained the dihydrate by saturating a not too conc. soln. of potassium dichromate with calcium hydroxide, passing a current of carbon dioxide through the clear liquid, and evaporating the soln. at 30°–40°. The crystals of the dihydrate are lemon-yellow. There is formed at the same time a brown crystalline crust of $K_2CrO_4.4CaCrO_4.2H_2O$, which is easily separated from the lemon-yellow crystals of the dihydrate. M. Gröger obtained it by evaporating on a water-bath an almost sat. soln. of potassium chromate containing 4 eq. of N-$CaCl_2$. M. Barre found that by the direct action of calcium chromate on soln. of potassium chromate at temp. below 45°, large rhombic prisms of the salt $K_2CrO_4.CaCrO_4.2H_2O$ are obtained. These, in contact with a soln. of potassium chromate at 60°, slowly disappear, and small, hexagonal prisms of the anhydrous salt, $K_2CrO_4.CaCrO_4$, are formed. Both these salts are decomposed by water. F. Stolba, and F. Mohr made some observations on this salt. G. N. Wyrouboff said that the crystals are dimorphous since there is an α-form occurring in yellow triclinic pinacoids $a:b:c=0\cdot6591:1:0\cdot4383$, and $\alpha=78°\ 16'$, $\beta=101°\ 3'$, and $\gamma=83°\ 8'$. The (101)-cleavage is complete, and the $(10\bar{1})$-cleavage is distinct. The sp. gr. is 2·411 at 15°, and the mol. vol. 160·5. The brown β-form also occurs in triclinic pinacoids with the axial ratios $a:b:c=0\cdot7516:1:0\cdot8807$, and $\alpha=86°\ 0'$, $\beta=94°\ 41'$, and $\gamma=81°\ 37'$. The (010)-cleavage is nearly complete. The sp. gr. is 2·596 at 15°, and the mol. vol. 149·3. The α-form is produced before the β-form. A. Rakowsky said that the α-form is not stable above 20°, and G. N. Wyrouboff added that it begins to give off water at 100°, and is completely dehydrated at 120°. A. Rakowsky found that the α-variety is less soluble than the β-form. Water at 0° and 15° dissolves respectively 23·06 and 25·06 parts of the α-form, and respectively 23·01 and 24·45 parts of the β-form. The heats of soln. of the α- and β-forms are, respectively, —6·99 Cals. and —5·45 Cals. H. G. F. Schröder gave 2·502 for the sp. gr. of the salt. E. Schweizer said that the salt loses water when heated, and becomes reddish-yellow while hot. It melts at a dull red-heat and forms, when cold, a crystalline cake. A. Duncan said that the salt which has been fused dissolves readily in water, but not in alcohol; and M. Gröger added that the salt is soluble in cold water without decomposition. E. Schweizer found that the aq. soln. decomposes on evaporation forming $K_2CrO_4.4CaCrO_4.2H_2O$. According to E. Schweizer, **potassium calcium quinquemonochromate,** $K_2CrO_4.4CaCrO_4.2H_2O$, is obtained, as indicated above. H. G. F. Schröder gave 2·787 for the sp. gr. In addition to the *dihydrate*, G. N. Wyrouboff obtained yellow *hemiheptahydrate*, $K_2CrO_4.4CaCrO_4.3\frac{1}{2}H_2O$, by saturating a cold, conc. soln. of potassium dichromate with calcium oxide, and allowing the filtered soln. to stand over sulphuric acid in a warm place. J. F. Bahr found that **potassium calcium seximonochromate,** $K_2CrO_4.5CaCrO_4$, separated during the evaporation of a soln. of calcium chloride and potassium chromate. The yellow, granular salt decrepitates when heated, and dissolves in water. M. Gröger could not prepare **ammonium calcium chromate.**

A. Osann found in the caliche deposits of Atacama, Chili, a salt which had a composition corresponding with **calcium iodatochromate,** $7Ca(IO_3)_2.8CaCrO_4$, and the mineral was called **dietzeite**—after A. Dietze, who had previously observed the complex salt in the same deposit. B. Gossner and F. Mussgnug's examination showed that the composition approximates $Ca(IO_3)_2.CaCrO_4$, and B. Gossner considered that the iodate and chromate furnish isomorphous mixtures. According to A. Osann, the colour of dietzeite is golden-yellow. The crystals are prismatic and tabular; but the mineral is commonly fibrous to columnar. The axial ratios of the monoclinic crystals are $a:b:c=1\cdot3826:1:0\cdot9515$, and $\beta=73°\ 28'$. B. Gossner and F. Mussgnug found that the X-radiograms correspond with $a=10\cdot6$ A., $b=7\cdot30$ A., $c=14\cdot03$ A., and $\beta=106°\ 32'$. This gives the axial ratios $a:b:c=1\cdot392:1:1\cdot922$; the elementary cell has the volume 997×10^{-24} c.c. According to A. Osann, the (100)-cleavage is imperfect; the lustre is vitreous; and the fracture, conchoidal. The optical character is positive and the optical axial angle $2G=87°$ to 88°. The hardness is 3 to 4; and the sp. gr. 3·698. B. Gossner and F. Mussgnug calculated 3·617 for the sp. gr. The salt is soluble in hot water, and the soln., on cooling, deposits crystals of $Ca(IO_3)_2.6H_2O$.

When a soln. of strontium chloride is treated with potassium chromate, **strontium chromate,** $SrCrO_4$, is precipitated. J. D. Smith observed that no precipitation occurs with dil. soln.; J. W. Döbereiner, that aq. soln. of strontium hydroxide gave no precipitate; and H. Kämmerer, and F. T. Frerichs, that no precipitation occurs if the soln. be acidified with acetic acid, but H. Caron and D. A. Raquet found that if the soln. be neutralized with ammonia, and treated with alcohol, strontium chromate is precipitated. A. de Schulten obtained the crystalline salt by dissolving 25 grms. of $Sr(HO)_2.4H_2O$ and 30 grms. of potassium dichromate in 100 c.c. of water heated on a water-bath, and adding drop by drop 0·3 per cent. ammonia. L. Bourgeois obtained the crystalline salt by melting a mixture of strontium chloride and sodium and potassium chromates as in the case of the calcium salt. The pale yellow powder consists of monoclinic prisms or plates which, according to A. de Schulten, have the axial ratios $a:b:c=0·9666:1:0·9173$, and $\beta=102° 43'$. E. Herlinger studied the structure of the crystals; and L. Bourgeois said that they are isomorphous with those of barium and calcium chromates, and with the sulphate. W. Autenrieth observed that strontium chromate furnishes bundles of long, slender, highly refracting needles, or, when separating from very dil. soln., it furnishes thick prisms of hexagonal habit. The latter appears to be a labile form which is slowly converted into the former. H. G. F. Schröder gave 3·353 for the sp. gr., and A. de Schulten, 3·895 at 15°. According to C. R. Fresenius, 100 parts of water at 15° dissolve 0·12 part of strontium chromate; and I. Meschtschersky, 0·119 part at 16°. F. Kohlrausch found that 100 c.c. of a soln. at 18° contain 0·12 grm. $SrCrO_4$; and C. Reichard, that water at 10° dissolves 0·465 per cent.; at 20°, 1·000 per cent.; at 50°, 2·417 per cent.; and at 100°, 3·000 per cent. F. Ransom made some observations on this subject. H. Caron and D. A. Raquet said that the solubility in water is lowered by the addition of alcohol. C. Reichard found that the chromate is freely soluble in hydrochloric, nitric, or aq. chromic acids; W. Autenrieth, and H. Caron and D. A. Raquet, that it is freely soluble in acetic acid—I. Meschtschersky said sparingly soluble. C. R. Fresenius observed that 100 c.c. of 29 per cent. alcohol dissolve 0·0132 grm. of strontium chromate; and 100 c.c. of 53 per cent. alcohol, 0·002 grm. E. Dumesnil said that it is readily soluble in a soln. of ammonium chloride, so that 100 c.c. of a sat. soln. of ammonium chloride, on boiling, easily dissolve a gram of the chromate. C. R. Fresenius observed that 100 parts of a 0·5 per cent. soln. of ammonium chloride at 15° dissolve 0·195 part of strontium chromate; 100 parts of 1 per cent. acetic acid, 1·57 part; and 100 c.c. of 0·75 per cent. acetic acid mixed with a little ammonium chromate, dissolve 0·287 part. F. Guthrie added that molten sodium nitrate dissolves 2·133 per cent. of strontium chromate. Strontium chromate has been used as a pigment—*lemon-yellow, strontian yellow, jaune de strontiane, giallo di stronziana,* and *amarillo di estronciana.*

M. Gröger prepared **potassium strontium chromate,** $K_2CrO_4.SrCrO_4$, by the action of an almost sat. soln. of potassium chromate containing 4 eq. of N-$SrCl_2$. M. Barre also prepared this salt. The yellow crystals are decomposed by water into the constituent salts. M. Barre found that the complex salt is stable at 11·5° in contact with a soln. containing 2·914 parts of potassium chromate per 100 parts of water; at 27·5°, 4·123 parts; at 50°, 5·942 parts; at 76°, 7·920 parts; and at 100°, 9·784 parts. He also obtained **ammonium strontium chromate,** $(NH_4)_2CrO_4.SrCrO_4$, by the action of a soln. of strontium chloride on one of ammonium chloride. The pale yellow crystals are decomposed by water.

When an aq. soln. of a barium salt, or baryta-water is treated with alkali mono- or di-chromate, a pale yellow precipitate of **barium chromate,** $BaCrO_4$, is deposited. J. D. Smith said that the precipitation with a barium salt is as delicate a test for chromate as it is for sulphates. F. T. Frerichs, and H. Kämmerer obtained a complete precipitation in the presence of acetic acid or sodium acetate. P. D. Chrustschuff and A. Martinoff observed that 12 per cent. of barium sulphate is converted into barium chromate by contact for 47 min. with a soln. containing potassium sulphate and potassium chromate in eq. proportions, whilst 1·5 per cent. of barium chromate is converted into barium sulphate in the same time in contact with a similar soln. The limits of the reaction do not attain more than 22 per cent. and 17 per cent. respectively, even after 40 to 45 hrs. M. Scholtz and R. Abegg found that at 100°, equilibrium between barium sulphate and potassium chromate in aq. soln. is established very slowly; it is reached more rapidly when a soln. of potassium sulphate acts on barium chromate. The ratio between the quantities of potassium chromate and sulphate in soln. when equilibrium is reached depends on the relative quantities of the solid barium salts, from which it appears that the precipitate consists of a solid soln. The relation $[K_2CrO_4][K_2SO_4] = 1{\cdot}3[BaCrO_4][BaSO_4]$ appears to hold. H. Rose found that an excess of alkali chromate will completely transform barium carbonate into the chromate; and F. J. Malaguti made observations on this subject, and J. Morris studied the precipitation of barium from a soln. of its chloride by the addition of a mixture of potassium carbonate and chromate. M. Scholtz and R. Abegg showed that in the equilibrium between potassium chromate and barium carbonate, the ratio of the conc. of potassium carbonate and chromate also varies in the same way as the ratio between the numbers of mols. of barium carbonate and chromate in the precipitate, but the two ratios are not proportional. There is, however, always relatively less chromate in the soln. than in the precipitate. Barium chromate and sulphate are about equally soluble, and both are much less soluble than the carbonate. A. Pool also studied this system. J. F. Bahr obtained crystalline barium chromate by decomposing barium dichromate with water; A. de Schulten, by heating on a water-bath a soln. of 20 grms. of barium nitrate in a litre of water mixed with 10 c.c. of nitric acid of sp. gr. 1·2, and adding 2 litres of a soln. of 10 grms. of potassium dichromate; and L. Bourgeois by melting 2 eq. of barium chloride with one eq. each of sodium, and potassium chromates. J. Milbauer found that when a mixture of barium oxide or carbonate and chromic oxide is heated to 480° in oxygen at 12 atm. press. there is a 52·8 per cent. conversion to chromate. J. A. Atanasiu found that in the electrometric titration of soln. of barium chloride soln. and potassium chromate there is a break corresponding with normal barium chromate. O. Ruff and E. Ascher studied the joint precipitation of lead and barium chromates; barium and strontium chromates; and barium sulphate and chromate; and O. Ruff, the X-radiograms.

The pale lemon-yellow barium chromate was found by H. Moser to become dark yellow when heated. L. Bourgeois said that the rhombic prisms are isomorphous with barium sulphate; and A. de Schulten gave for the axial ratios of the rhombic plates $a:b:c = 0{\cdot}8038:1:1{\cdot}2149$. F. Rinne studied the crystals of barium chromate; and M. Copisarow observed tree-like, dendritic forms are produced when the precipitate is slowly formed. The sp. gr. observed by H. G. F. Schröder is 4·296–4·304; C. H. D. Bödecker, 3·90 at 11°; E. Schweizer, 4·5044; A. Schafarik, 4·49 at 23°; L. Bourgeois, 4·60; and A. de Schulten, 4·498 at 15°. P. Bary, and J. Precht found that the salt is not fluorescent when exposed to X-rays. F. Kohlrausch gave for the sp. conductivity of sat. soln. $0{\cdot}0_5114$ mho at $-0{\cdot}88°$; $0{\cdot}0_5297$ mho at 16·07°, $0{\cdot}0_5317$ mho at 17·42°; and $0{\cdot}0_5499$ mho at 28·08°. The solubility of the salt in water is very small; F. Kohlrausch and co-workers calculated from observations on the electrical conductivity, the following solubilities, S grms. per litre:

	−0·88	16·07°	17·42°	18°	28·08°
S . .	2·04	3·37	3·48	3·53	4·36

For the equilibrium between barium chromate and dichromate, *vide supra*, chromic acid. I. Meschtschersky found that a litre of water dissolved 4·3 mgrms. at 100°. C. R. Fresenius said that at 0°, a litre of water dissolves 1·19 mgrms. The salt is less soluble after it has been ignited. E. Schweizer said that in that state a litre of water dissolves 0·62 mgrm. L. M. Henderson and F. C. Kracek pointed out that the solubilities of the alkaline earth chromates decrease as the at. wt. of the alkaline earth metal. Thus, at 15°, the solubilities of the anhydrous calcium, strontium and barium chromates are of the order 25, 1·2, and 0·0033 grms. per litre respectively. The solubility of **radium chromate** seems to follow the rule, and a separation of radium and barium can be effected by fractional precipitation as chromates. The partition factor for acidic soln. is about 15·5.

The soln. of barium chromate in hydrochloric, or nitric acid or in an excess of chromic acid, was found by J. F. Bahr, H. Caron and D. A. Raquet, and K. Preis and B. Rayman to become orange-red owing to the formation of dichromate, but the monochromate is reprecipitated from this soln. by ammonia. The statement with reference to the solubility in soln. of chromic acid was disputed by L. Schulerud, and W. Autenrieth. E. Schweizer said that the salt is insoluble in a soln. of potassium dichromate, and 100 parts of a 10 per cent. soln. of chromic acid dissolve 0·055 part of chromate. When sulphur dioxide is passed over heated barium chromate W. R. Hodgkinson and J. Young found that chromium sulphate is formed as the chromate is decomposed. N. W. Fischer observed that barium chromate is not decomposed by cold sulphuric acid, but is decomposed with difficulty by the hot acid; he also stated that aq. soln. of sulphates do not affect the chromate, and the action is only slight with hot soln. H. Schwarz found that about a quarter mol is decomposed by a mol of conc. sulphuric acid to form, according to L. Bourgeois, barium sulphate and chromium trioxide. Observations by P. D. Chrustschoff and A. Martinoff, M. Scholtz and R. Abegg are indicated above. The transformation of the chromate into carbonate by the fusion with sodium carbonate, or by digestion with a soln. of the carbonate, was discussed by H. Rose, F. J. Malaguti, M. Scholtz and R. Abegg—*vide supra*. K. W. Flöroff gave $1{\cdot}6\times10^{-11}$ for the solubility product at 18°. According to H. Golblum, the equilibrium constant $K=[K_2CO_3]/[K_2CrO_4]$ in the reaction: $K_2CO_3+BaCrO_4\rightleftharpoons BaCO_3+K_2CrO_4$, is not constant but decreases to a minimum value. The deviation from the simple mass law is ascribed to the ionization of the salts. The heat of the reaction, calculated from the equilibrium constants at 25° and 40°, is 5997 cals. E. Carrière and P. Castel found that the equilibrium constant $K=[CrO_4]^2[H]^2/[Cr_2O_7]$ with barium chromate in acid soln. is 3×10^{-15}.

B. Guerini observed that $0{\cdot}22\times10^{-4}$ gram-equivalent of barium chromate are dissolved by a litre of 45 per cent. alcohol, and A. Naumann observed that it is insoluble in acetone, and in methyl acetate. I. Meschtschersky, and H. Baubigny said that the chromate is soluble in acetic acid; while H. Caron and D. A. Raquet said that barium chromate is insoluble in acetic acid and soln. of alkali chromate, but partially soluble in a mixture of dichromate and acetic acid. According to C. R. Fresenius, the presence of acetic acid increases the solubility of barium chromate, for 100 parts of water containing one part of acetic acid dissolve 0·0027 part of chromate. E. Schweizer said that 100 parts of 5 per cent. acetic acid dissolve 0·02725 part of chromate, and with 10 per cent. acetic acid, 0·0503 part. C. R. Fresenius said that ammonium salts also make the chromate more soluble, thus 100 parts of water containing 0·5 per cent. of ammonium chloride dissolve 0·00435 part of the chromate; water with 0·5 per cent. of ammonium nitrate dissolves 0·00222 part of chromate; water with 0·75 per cent. of ammonium acetate dissolves 0·002 part of chromate; and water with 1·5 per cent. of ammonium acetate dissolves 0·00417 part of chromate. E. Fleischer found that barium chromate is readily soluble in soln. of alkali tartarate or citrate; L. Bourgeois that it is decomposed with difficulty by alkali hydroxides; and F. Guthrie that molten sodium nitrate dissolves 0·205 per cent. $BaCrO_4$. K. W. Flöroff studied the adsorption of potassium chromate by barium sulphate, and showed that the reaction, particularly for conc. soln., is complex—probably $2BaSO_4+K_2CrO_4=BaSO_4.BaCrO_4+K_2SO_4$. L. Kahlenberg and W. J. Trautmann observed that when mixed with silicon, there is a strong reaction at a cherry-red-heat, and in the electric arc. C. Zerr and G. Rübencamp mentioned the use of barium chromate as a pigment—*ultramarine yellow, lemon yellow, permanent yellow, jaune de baryte, giallo di barite, amarillo di barita, oltremare giallo, outremer jaune, amarillo ultrames, Citrongelb.* M. A. Iljinsky and co-workers studied the adsorption of barium chromate by silk, wool, and cotton fibres.

M. Gröger prepared **potassium barium chromate,** $K_2CrO_4.BaCrO_4$, by shaking an almost sat. soln. of potassium chromate with a cold, sat. soln. of barium chloride. The pale yellow granules are decomposed by water. M. Barre also prepared this salt. M. Gröger also made **ammonium barium chromate** by precipitation with soln. of ammonium chromate and barium chloride. The precipitate is at first amorphous, but soon forms six-sided plates. The salt is decomposed by water. L. Bourgeois reported **barium strontium chromate,** $BaSr(CrO_4)_2$, to be formed in prismatic crystals by the process used for strontium calcium chromate—*vide supra ;* similarly also with **barium calcium chromate,** $BaCa(CrO_4)_2$. L. H. Duschak found that a crystalline precipitate of barium and strontium chromates of definite composition is formed in a sat. soln. of barium chromate containing given conc. of strontium chromate and acetic acid. Diffusion takes place within this substance, and that, therefore, it must either be regarded as a solid soln., or else diffusion must be recognized as a possible property of isomorphous mixtures. L. M. Henderson and F. C. Kracek [12] discussed the separation of radium and barium by the fractional precipitation of barium chromate and **radium chromate.**

A. Atterberg [13] found that beryllium hydroxide dissolved in an aq. soln. of chromic acid to form a deep red liquid from which no crystals can be obtained ; and that when a soln. of beryllium sulphate is treated with potassium chromate, the precipitate first formed dissolves with stirring, and finally there is deposited a yellow basic salt. J. C. G. de Marignac treated soln. of potassium dichromate with beryllium sulphate and obtained a precipitate of variable composition. A. Atterberg found that beryllium carbonate is decomposed by a soln. of potassium dichromate, carbon dioxide is evolved, and a basic chromate is formed. This when washed and dried gives a pale yellow powder approximating $14BeO.CrO_3.23H_2O$. It loses 5 mols. of water at 100° ; 16 mols. at 300° ; and all is lost at dull redness. At a higher temp. oxygen is given off. B. Glassmann obtained **beryllium dodecahydroxychromate,** $6Be(OH)_2.BeCrO_4$, as a yellow powder by heating the normal chromate with water, or by treating a soln. of beryllium sulphate with ammonium chromate. It is insoluble in water, but soluble in chromic acid soln. Normal **beryllium chromate,** $BeCrO_4.H_2O$, was obtained by neutralizing a conc. soln. of chromic acid with beryllium carbonate, and evaporating the liquid. The reddish-yellow, monoclinic plates are hydrolyzed by water. B. Bleyer and A. Moormann could not obtain either of the two salts described by B. Glassmann. The precipitation of beryllium sulphate by potassium chromate yields impure, amorphous products of varying composition, whilst the precipitate from the chloride has the composition $15BeO.CrO_3.12H_2O$, independently of the proportions of the reacting substances. Beryllium hydroxide and chromic acid yield only resinous masses, but the clear soln. contains beryllium and chromium in the ratio 1 : 1. N. A. Orloff obtained $9BeO.BeCrO_4.16H_2O$ and $20H_2O$, and $14BeO.BeCrO_4.31H_2O$, from a soln. of beryllium sulphate and potassium chromate ; $12BeO.BeCrO_4.16H_2O$ from a soln. of beryllium hydroxide in chromic acid and potassium chromate ; and $5BeO.BeCrO_4.14H_2O$, as a precipitate by adding alcohol to a soln. of beryllium hydroxide in chromic acid. Hence, beryllium chromate is gradually hydrolyzed by water without forming any definite basic salt. H. C. Creuzberg prepared beryllium tridecoxychromate, $BeCrO_4.13BeO.23H_2O$, by precipitation.

L. N. Vauquelin [14] prepared **magnesium chromate,** $MgCrO_4$, by crystallization from a soln. of magnesia in chromic acid. J. Milbauer observed an 82·7 per cent. conversion to chromate when chromic oxide mixed with magnesium oxide or carbonate is heated to 480° in oxygen at 12 atm. press. The orange-yellow, six-sided prisms of the chromate crystallized in aq. soln. were said by H. Kopp to be isomorphous with magnesium sulphate, and his analysis corresponded with *heptahydrate*, $MgCrO_4.7H_2O$. A. Murmann gave for the axial ratios of the rhombic, bisphenoidal crystals $a : b : c = 0·9901 : 1 : 0·5735$. The (010)-cleavage is perfect. W. J. Grailich gave for the optic axial angle $2V = 75° 28'$. The optical character is negative. E. Dittler obtained overgrowths with magnesium sulphate. H. G. K. Westenbrink found that the rhombic bisphenoidal crystals have four mols. in unit cell, and that the dimensions are $a = 11·89$ A., $b = 12·01$ A., and $c = 6·89$ A. Observations on the crystals were made by H. Dufet, and L. Longchambon ;

C. Gaudefroy studied the corrosion figures; and A. Fock, the solid soln. of the heptahydrates of magnesium chromate and sulphate. H. Kopp gave 1·66 for the sp. gr. at 15°; C. H. D. Bödeker, 1·75; and F. W. Clarke, 1·761 at 16°. F. Mylius and R. Funk observed that a sat. soln. containing 4·2 per cent. $MgCrO_4$ had a sp. gr. 1·422; A. Heydweiller found the sp. gr. at 18°/18° of soln.:

$MgCrO_4$.	0·1234*N*-	0·247*N*-	0·617*N*-	1·1234*N*-	2·468*N*-	4·936*N*-
Sp. gr. .	1·00857	1·01710	1·04178	1·0818	1·1596	1·3052

K. F. Slotte found the sp. gr. of soln. of magnesium chromate with 12·31, 21·86, and 27·71 per cent. of chromate to be respectively 1·0886 at 13·6; 1·1641 at 14·5°; and 1·217 at 13·6°; and the viscosities (water 100) to be respectively 151·8, 227·8, and 317·7 at 10°; 115·4, 170·9, and 235·6 at 20°; 92, 134·7, and 182·8 at 30°; and 75, 108·6, and 145·5 at 40°. W. Kohlrausch said that 100 c.c. of a sat. soln. at 18° contain 60 grms. $MgCrO_4$; and G. N. Wyrouboff found that the heptahydrate lost 2 mols. of water in air, 3 mols. at 120°; but expulsion of the last mol. of water is attended by the decomposition of the salt. M. R. Nayar and co-workers observed that very little chromate is formed when a mixture of magnesia and chromic oxide is heated below 600°; at 650°, magnesium chromate decomposes into basic chromites (*q.v.*). H. Topsöe and C. Christiansen found the indices of refraction for the *D*-line to be $\alpha=1·5211$, $\beta=1·5500$, and $\gamma=1·5680$; while for the *C*-line, $\alpha=1·5131$, $\beta=1·4315$, and $\gamma=1·5633$. A. Fock gave for the refractive indices, μ, and the optic axial angle, $2V$, of mixtures of magnesium sulphate and chromate containing the eq. per cent. of $MgCrO_4.7H_2O$,

	$MgCrO_4 . 7H_2O$	0	52	15·8	18·5	31·6	35·9	43·7	100 per cent.
μ	α . .	0·4319	1·4353	1·4388	1·4408	1·4457	1·4543	1·6432	1·5221
	β . .	1·4519	1·4579	1·4618	1·4632	1·4727	1·4778	1·4934	—
	γ . .	1·4602	1·4635	1·4666	1·4697	1·4844	1·4881	—	1·5680
$2V$	. .	51° 28′	53° 32′	53° 58′	55° 40′	57° 16′	60° 14′	69° 52′	75° 28′

P. Walden gave for the eq. conductivity, λ mho, at 25° with a mol of the salt in v litres:

v . . .	32	64	128	256	512	1024
λ . . .	80·6	90·6	98·9	107·2	114·3	119·9

while H. Clausen, and A. Heydweiller obtained for conc. soln., at 18°:

v . . .	0·203	0·405	0·81	1·62	4·05	8·1
λ . . .	12·23	24·85	34·17	41·07	48·09	54·86

W. J. Grailich and V. von Lang found the diamagnetism to be strongest in the direction of the (010)-axis. M. Wein studied the electrical conductivity. A. Naumann said that the salt is soluble in acetone. G. N. Wyrouboff prepared the *pentahydrate*, $MgCrO_4.5H_2O$, from the heptahydrate as indicated above; or by crystallizing an aq. soln. above 30°. The yellow crystals are stable, and do not effloresce in air. They are triclinic pinacoids with the axial ratios $a:b:c=0·5883:1:0·5348$, and $\alpha=82°\ 43'$, $\beta=108°\ 14'$, and $\gamma=103°\ 51'$. They are isomorphous with pentahydrated cupric sulphate. No cleavage was observed. The sp. gr. is 1·954. For the action of heat, *vide supra.*

M. Gröger prepared **ammonium magnesium chromate,** $(NH_4)_2Mg(CrO_4)_2.6H_2O$, from soln. of ammonium chromate and magnesium chloride; and F. J. Malaguti and M. Sarzeau, by adding ammonia to a soln. of magnesium chromate in aq. chromic acid until the hydroxide begins to separate, and then evaporating. The pale yellow crystals were found by A. Murmann to be monoclinic prisms with the axial ratios $a:b:c=0·7511:1:0·4931$, and $\beta=106°\ 31'$; and M. W. Porter, $0·7517:1:0·4935$ and $\beta=106°\ 07'$. A. E. H. Tutton and M. W. Porter found the topic axial ratios $\chi:\psi:\omega=6·3751:8·4811:4·1761$. The optic axial angles:

	red-light	Li-	*C*-	Na-	Tl-	Cd-lines
$2E$ . . .	16° 29′	9° 50′	14° 29′	45° 8′	66° 1′	77° 43′
$2V$ . . .	10° 47′	6° 15′	8° 54′	26° 53′	38° 57′	44° 37′

They also investigated the effect of temp. on these angles. M. W. Porter found with 0, 43·85, 72·52, and 100 per cent. $(NH_4)_2Mg(CrO_4)_2.6H_2O$, the axial ratios 0·7499 : 1 : 0·4935, and β=106° 15′; 0·7476 : 1 : 0·4928, and β=106° 32′; 0·7451 : 1 : 0·4930, and β=106° 55′; and 0·7409 : 1 : 0·4924, and β=107° 6′ respectively; and the respective refractive indices α=1·6363, β=1·6371, γ=1·6531; α=1·554, β=1·557, γ=1·560; α=1·491, β=1·493, γ=1·495; and α=1·4716, β=1·4730, γ=1·4786. S. Rosch and M. Stürenburg studied the optic axial angles. F. W. Clarke gave 1·84 for the sp. gr. at 16°; and M. W. Porter, 1·835 at about 16°. The mol. vol. is 215·92. C. Schaefer and M. Schubert observed in the ultra-red reflection spectrum a complex maximum at 11·3μ to 11·42μ; and in polarized light the maximum falls into three groups—11·46μ parallel to the a-axis, 11·28μ parallel to the b-axis, and 10·36μ parallel to the c-axis. A. E. H. Tutton and M. W. Porter found for the indices of refraction:

	Li-	C-	Na-	Tl-	Cd-light
α . . .	1·6248	1·6265	1·6363	1·6489	1·6571
β . . .	1·6250	1·6267	1·6371	1·6509	1·6602
γ . . .	1·6390	1·6411	1·6531	1·6687	1·6799

The refractive indices at 80° were about 0·0023 lower than for ordinary temp. The optical properties of isomorphous mixtures of ammonium magnesium sulphate and chromate were examined. F. Rüdorff's diffusion experiments showed that the salt is more or less dissociated in aq. soln. G. Canneri prepared **guanidine magnesium chromate,** $(CH_5N_3)_2.H_2CrO_4.MgCrO_4.6H_2O$, isomorphous with the sulphate. A. Stanley evaporated a soln. obtained by treating a soln. of sodium dichromate with a magnesium salt, and obtained yellow, four-sided prisms and plates of **sodium magnesium chromate,** $Na_2CrO_4.MgCrO_4.3H_2O$. The salt gives off all its water below 200° leaving the reddish-brown, pulverulent anhydride. The *trihydrate* is freely soluble in water and alcohol, but insoluble in ether.

T. Thomson, and E. F. Anthon prepared **potassium magnesium chromate,** $K_2CrO_4.MgCrO_4.2H_2O$, by evaporating a soln. of potassium dichromate mixed with magnesia; M. Gröger, by treating an almost sat. soln. of potassium chromate with a soln. of magnesium chloride. G. N. Wyrouboff said that the *dihydrate* is obtained if the soln. be evaporated over 18°. The triclinic, pinacoidal crystals were found by G. N. Wyrouboff to have the axial ratios $a:b:c$=0·6551 : 1 : 0·4326, and α=84° 35′, β=102° 44′, and γ=86° 38′. Twinning occurs about the (101)-, $(10\bar{1})$-, and (100)-planes; and the (101)- and $(10\bar{1})$-cleavages are distinct. The optical character is negative. H. G. F. Schröder gave 2·600 for the sp. gr.; E. F. Anthon, 2·59 at 19°; and G. N. Wyrouboff, 2·602 at 16°, and for the mol. vol. 142·5. E. F. Anthon observed that when the salt is heated, it becomes orange-yellow, and melts at dull redness forming a dark red liquid; and E. Schweizer represented the decomposition at a red-heat by $2K_2Mg(CrO_4)_2=2K_2CrO_4+MgO+Mg(CrO_2)_2+3O$. G. Viard said that not $MgO.Cr_2O_3$ but rather $2MgO.Cr_2O_3$ and $5MgO.4Cr_2O_3$ are produced. E. Schweizer said that 100 parts of water dissolve 28·2 parts of the salt at 20°, and 34·3 parts at 60°; and M. Gröger, that the salt is not decomposed by cold water. The salt is insoluble in alcohol. S. H. C. Briggs reported that the *hexahydrate*, $K_2Mg(CrO_4)_2.6H_2O$, is formed by cooling a conc. soln. to −10°. The lemon-yellow crystals can be washed with alcohol and ether. When dried in air at 8°–10°, the salt loses 4 mols. of water. G. N. Wyrouboff said that the hexahydrate is formed by evaporating the soln. below 1·8°. C. von Hauer could not make the hexahydrate. A. Duffour found that the hexahydrate can be obtained if the two chromates are dissolved separately in equimolar proportions in two and a half times their weight of warm water, and the soln. are mixed, filtered, and left to evaporate at a temp. not exceeding 15°. After several days, the hexahydrate separates in tabular crystals, which should be removed at once. The crystals after five or six hours begin to change slowly into the dihydrate. This dehydration is far more rapid at 120° but always stops at the dihydrate. The hexahydrate is thus known only in a metastable state even 10°. The crystals are monoclinic and have the axial ratios $a:b:c=0.7521:1:0.4984$, and $\beta=103° 54'$. Monoclinic crystals of the hexahydrate, in solid soln. with the hexahydrated potassium magnesium sulphate, can be obtained by the evaporation at 20° of a soln. with 3 mols of the complex sulphate to one mol of the complex chromate. A. Duffour studied the triclinic crystals of solid soln. of hexahydrated potassium magnesium chromate and sulphate.

S. H. C. Briggs prepared **rubidium magnesium chromate,** $Rb_2CrO_4.MgCrO_4.6H_2O$, by a process analogous to that used for the potassium salt. The lemon-yellow crystals are stable in air. T. V. Barker also prepared this salt and found that the axial ratios of the monoclinic crystals are $a:b:c=0.7558:1:0.4950$, and $\beta=104° 55'$; M. W. Porter gave 0·7540 : 1 : 0·4960 and $\beta=104° 52'$. A. E. H. Tutton and M. W. Porter gave for the optic axial angle :

	Li-	C-	Na-	Tl-	Cd-light
$2V$ . .	88° 27′	88° 4′	86° 33′	84° 31′	83° 15′

They also gave for the topic axial ratios $\chi:\psi:\omega=6.3403:8.4246:4.1727$; and the sp. gr. 2·466 at 20°/4°. M. W. Porter gave 2·463 at about 16°, and the mol. vol. at 20° is 215·48 ; F. A. Henglein gave 217·0. M. W. Porter found that the indices of refraction are $\alpha=1.6363$, $\beta=1.6371$, and $\gamma=1.6528$. A. E. H. Tutton and M. W. Porter found for the indices of refraction :

	Li-	C-	Na-	Tl-	Cd-light
α . .	1·6105	1·6118	1·6217	1·6342	1·6426
β . .	1·6208	1·6221	1·6330	1·6466	1·6561
γ . .	1·6310	1·6326	1·6435	1·6517	1·6672

The refractive indices, α, β, and γ, diminish respectively by 0·0019, 0·0024, and 0·0025 on raising the temp. to 80°. M. W. Porter examined the optical properties of isomorphous mixtures of ammonium and rubidium magnesium chromates. M. W. Porter showed that the ammonium and rubidium magnesium chromates are completely isomorphous. Selecting some of the observed data for the isomorphous mixtures containing 0, 35·35, 74·05, and 100 per cent. of the ammonium salt, the axial ratios were 0·7540 : 1 : 0·4960, and $\beta=104° 52'$; 0·7526 : 1 : 0·4928, and $\beta=105° 23'$; 0·7522 : 1 : 0·4931, and $\beta=105° 47'$; and 0·7517 : 1 : 0·4935, and $\beta=106° 9'$ respectively ; the sp. gr., 2·463, 2·211, 1·998, and 1·835 respectively ; and the indices of refraction $\alpha=1.6216$, $\beta=1.6330$, and $\gamma=1.6439$; $\alpha=1.6268$, $\beta=1.6371$, and $\gamma=1.6468$; $\alpha=1.6330$, $\beta=1.6368$, and $\gamma=1.6493$; and $\alpha=1.6363$, $\beta=1.6371$, and $\gamma=1.6538$ respectively. S. H. C. Briggs prepared **cæsium magnesium chromate,** $Cs_2Mg(CrO_4)_2.6H_2O$, by the method employed for the potassium salt. The cæsium salt is rather more stable than the rubidium salt. T. V. Barker gave for the axial ratios of the monoclinic crystals $a:b:c=0.7420:1:0.4886$, and $\beta=106° 7'$. A. E. H. Tutton and M. W. Porter gave for the optic axial angles :

	Li-	C-	Na-	Tl-	Cd-light
$2E$ . .	131° 3′	131° 27′	132° 55′	133° 22′	—
$2V_a$ . .	67° 9′	67° 7′	67° 3′	66° 33′	65° 57′

The topic axial ratios are $\chi:\psi:\omega=6.4441:8.6718:4.2388$; the sp. gr. is 2·747 at 20°/4° ; and the mol. vol. 227·62 ; F. A. Henglein gave 229·2. A. E. H. Tutton and M. W. Porter found the indices of refraction to be :

	Li-	C-	Na-	Tl-	Cd-light
α . .	1·6257	1·6271	1·6369	1·6493	1·6578
β . .	1·6310	1·6324	1·6425	1·6552	1·6640
γ . .	1·6424	1·6438	1·6547	1·6683	1·6778

A rise of temp. to 80° results in the reduction of the indices by about 0·0026.

Normal **zinc chromate,** $ZnCrO_4$, is not easy to prepare, for, if a large proportion of water be present, a basic salt is formed ; and if very conc. soln. are employed at a high temp., oxygen may be evolved. J. Milbauer[15] said that there is a 72 per cent. conversion to chromate when a mixture of chromic oxide and zinc oxide or carbonate is heated to 480° in oxygen at 12 atm. press. S. H. C. Briggs did not succeed in preparing the normal chromate in a non-aqueous solvent. J. Schulze obtained normal zinc chromate by heating the dichromate with zinc hydroxide in a sealed tube to 200°; and S. H. C. Briggs recommended heating for 3 hrs. at 220° in a sealed tube a mixture of 4·5 grms. CrO_3, 4·5 grms. zinc carbonate with 70 per cent. ZnO, and 5 c.c. of water. According to M. Gröger, by shaking zinc oxide with a soln. of chromic acid, in different proportions, and after a few days, determining the compositions of the filtrate, and precipitate, the composition of the soln. is found to vary continuously, Fig. 49, but the composition of the solid phase shows discontinuities, Fig. 49; if the concentrations of the soln. be expressed in mols per litre, the solid phases correspond with

CrO . .	0·00010	0·1140	0·6660	1·92	4·62
ZnO_3 .	0·00016	0·0720	0·3720	1·03	2·41
Solid.	$4ZnO.CrO_3.3H_2O$	$3ZnO.CrO_3.2H_2O$	$2ZnO.CrO_3.1\frac{1}{2}H_2O$	$3ZnO.2CrO_3$	

Beyond the limit $CrO_3 : ZnO = 4·62 : 2·41$, the solid phase is the *monohydrate*, $ZnCrO_4.H_2O$. The soln. also contained some zinc mono- and di-chromates. All the solids were crystalline excepting the 3 : 2 : 1 compound. The monohydrated monochromate did not lose water at 125°; and it was not found possible to convert it into the insoluble, anhydrous salt.

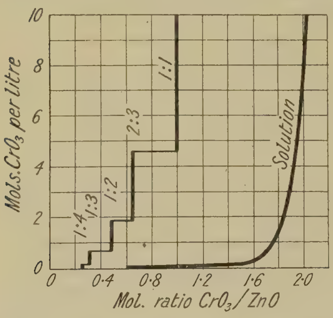


FIG. 49.—Equilibrium Conditions in the System: $ZnO–CrO_3–H_2O$ at 25°.

According to J. Schulze, normal zinc chromate furnishes microscopic, lemon-yellow, prismatic crystals, which are insoluble in water, easily soluble in acids, and are decomposed by boiling with water to form soluble dichromate and an insoluble basic chromate. M. Gröger's observations on the action of water on the monohydrate are summarized in Fig. 49. H. S. Taylor and G. I. Lavin studied the action of activated hydrogen on the chromate. E. C. Franklin said that zinc chromate is insoluble in liquid ammonia; and A. Naumann, that it is insoluble in acetone. M. Gröger said that the product of the action of zinc chloride on an excess of ammonium chromate is probably **zinc amminochromate,** $ZnCrO_4.NH_3.H_2O$. This *monohydrate* is decomposed by water; and forms zinc chromate when heated giving off nitrogen and water. L. Bieler prepared the *trihydrate* of **zinc tetramminochromate,** $ZnCrO_4.4NH_3.3H_2O$, by dissolving the basic salt in the smallest amount of aq. ammonia, and adding to the filtrate 2 or 3 times its vol. of absolute alcohol. The crystals are then dissolved in aq. ammonia, some ammonium chloride is added, and the salt again precipitated with alcohol. The rhombic plates rapidly effloresce forming a yellow powder. The salt is freely soluble in aq. ammonia, and in dil. acids; but it is decomposed by water with the separation of a basic salt. F. J. Malaguti and M. Sarzeau obtained the *pentahydrate*, $ZnCrO_4.4NH_3.5H_2O$, by allowing a basic salt to stand for 12 hrs. in a closed flask with sat. aq. ammonia. The salt is precipitated from the clear soln. by adding alcohol. The yellow cubes are decomposed by water; they are soluble in aq. ammonia; and insoluble in alcohol and ether. By mixing the 4 : 1 : 5 basic chromate with an excess of aq. ammonia, and adding alcohol, F. J. Malaguti and M. Sarzeau obtained yellow masses of acicular crystals of **zinc decamminochromate,** $2ZnO.3CrO_3.10NH_3.10H_2O$.

A number of basic salts has been reported; and a number of these, of indefinite composition, forms the so-called *zinc yellow, zinc chrome, Zinkgelb, jaune de zinc,* or *yellow ultramarine* which is employed as a pigment. T. Thomson prepared the colour in 1825; and W. A. Lampadius, in 1829. C. O. Weber prepared a bright yellow, flocculent powder by treating a soln. of zinc sulphate and sodium carbonate with potassium chromate. Its composition approximated $4ZnO.3CrO_3.nH_2O$. M. Prud'homme and F. Binder obtained a basic salt by heating zinc hydroxide with a soln. of potassium chromate and dichromate. The zinc yellows have been discussed by L. Bock, J. G. Gentele, G. Zerr and G. Rübencamp, F. Rose, S. Tschelnitz, etc. The colour was discussed by W. Ackroyd. The conditions of equilibrium of the basic salts are indicated in Fig. 49. M. Gröger, and B. Skormin obtained **zinc trioxychromate,** $4ZnO.CrO_3.3H_2O$, as a *trihydrate,* by mixing soln. of zinc chloride and sodium chromate at ordinary temp.; by treating the basic potassium or ammonium zinc chromates with hot water; and by the action of chromic acid on zinc oxide in accord with the conditions indicated in Fig. 49. J. Prüssen and H. Philippona obtained it by boiling the precipitate obtained by mixing zinc sulphate and potassium chromate soln. with much water for a long time. F. J. Malaguti and M. Sarzeau said that the *pentahydrate* is formed when zinc carbonate is treated with a soln. of chromic acid. H. Kopp added that if the chromic acid contains sulphuric acid as impurity, the precipitate will be contaminated with basic zinc sulphate. M. Gröger obtained **zinc dioxychromate,** $3ZnO.CrO_3.2H_2O$, by the action of chromic acid on zinc oxide in accord with the conditions indicated in Fig. 49. M. Gröger, and B. Skormin likewise prepared **zinc oxychromate,** $2ZnO.CrO_3.1\frac{1}{2}H_2O$. The *hemitrihydrate* was also prepared by T. Thomson, A. Bensch, and J. Prüssen and H. Philippona by the action of a soln. of zinc sulphate on one of potassium chromate. L. Vanino and F. Ziegler added a sat. soln. of chromic acid to a mol. eq. of zinc oxide suspended in water, constantly agitated. The zinc oxide passed into soln. with a rise of temp. After a time an orange or brownish-yellow product separated approximating $ZnO.ZnCrO_4.nH_2O$. S. H. C. Briggs obtained the *monohydrate* as a yellow, crystalline powder by heating for 3 hrs. in a sealed tube a mixture of 4 grms. chromium trioxide, 3 grms. of zinc oxide, and 20 grms. of water. M. Gröger also prepared **zinc oxybischromate,** $3ZnO.2CrO_3.H_2O$, by the action of chromic acid on zinc oxide in accord with the conditions indicated in Fig. 49.

It is doubtful if the **potassium zinc chromates** or the **ammonium zinc chromates** have been prepared. The products which have been reported may be adsorption products of the basic salts. M. Gröger reported products with the mol. ratios $K_2O : ZnO : CrO_3 : H_2O = 1:5:4:6$; $1:4:4:3$; and $1:1:2:2$. L. Vanino and F. Ziegler found that on mixing a sat. soln. of potassium dichromate at 100° with zinc sulphate soln. sat. at 39°, so that the ratio $CrO_3 : ZnO$ is $1:1$, or by pouring one soln. into the other, in either case, a deep yellow precipitate is formed; which after filtering and washing approximates **potassium zinc trioxybischromate,** $2K_2O.3ZnO.2ZnCrO_4$. It is supposed that the zinc chromate first formed hydrolyzes when washed with water, forming this basic chromate or a mixture of basic chromates. He showed that the action of an excess of zinc chloride in an aq. soln. of N- or $3N$-K_2CrO_4 leads to the formation of a yellow, granular precipitate, which has the composition $4ZnO.K_2O.4CrO_3.3H_2O$. By repeated treatment with hot water, this is converted into the insoluble basic zinc chromate, $ZnCrO_4.3Zn(OH)_2$, which is a dark yellow powder. When fused, the zinc potassium chromate evolves oxygen, the residue consisting of potassium chromate and insoluble violet zinc chromite, $8ZnO.3Cr_2O_3$. The proportion of potassium, and, to a less extent, that of chromium, is increased by the use of an excess of the potassium chromate; with N-soln., the precipitate has the mol. composition $ZnO.0{\cdot}394K_2O.1{\cdot}094CrO_3$; with $3N$-soln., $ZnO.0{\cdot}486K_2O.1{\cdot}222CrO_3$. When treated with hot water, these precipitates yield the foregoing basic zinc chromate. These precipitates are of a deeper yellow than that formed in presence of excess of zinc salt, but after prolonged contact (2 weeks) with the mother-liquor they assume the colour and composition of the latter. The action of zinc chloride on sodium chromate leads to the formation of basic zinc chromate, $ZnCrO_4.3Zn(OH)_2$, which is obtained as a horny mass. Ammonium chromate and excess of zinc chloride give rise to a dark yellow, granular precipitate, $ZnO.0{\cdot}279(NH_4)_2O.0{\cdot}822CrO_3$, which is possibly a mixture, and is decomposed by cold water. The orange-yellow precipitate, formed by the action of an excess of ammonium chromate on zinc chloride, is stable to water or its mother-liquor and has the composition $(NH_4)_2CrO_4.ZnCrO_4.Zn(OH)_2$. When strongly heated, it decomposes suddenly, evolving nitrogen and water vapour; the residue is a powder consisting of zinc oxide and chromite, $2ZnO.Cr_2O_3$. These salts were discussed by J. J. Berzelius, C. Freese, J. Prüssen and H. Philippona, C. O. Weber, B. Skormin, and L. Bock. According to S. H. C. Briggs, **ammonium zinc diamminobischromate,** $(NH_4)_2.Zn(CrO_4)_2.2NH_3$, is formed in lemon-yellow crystals by adding an excess of ammonium chloride or nitrate to a soln. of 10 grms. of zinc hydroxide in 20 grms. of chromium trioxide in a little water and all diluted to 200 c.c. M. Gröger obtained it in prismatic crystals by the action of ammonium chromate on zinc chloride in the presence of a large excess of ammonia. M. Gröger also reported **ammonium zinc triamminosexichromate,** $(NH_4)_4Zn_4(CrO_4)_6.3NH_3$, in orange-yellow crystals, by dropping 10 c.c. of $2M$-$ZnCl_2$ into 50 c.c. of a cold, sat. soln. of ammonium chromate.

J. Schulze prepared normal **cadmium chromate,** $CdCrO_4$, by heating in a sealed tube at 200°, a mixture of cadmium dichromate and cadmium hydroxide. The pale orange-coloured powder is insoluble in water, and soluble in acids. It gradually decomposes when boiled with water. S. H. C. Briggs obtained it by heating a mixture of 3·5 grms. cadmium oxide, 3·6 grms. chromium trioxide, and 20 c.c. of water in a sealed tube at 200° for 3 hrs. He said that the yellow powder consisting of prismatic crystals is insoluble in a hot, conc. soln. of cadmium sulphate. G. Viard said that the salt is very stable and begins to decompose at dull redness. When the filtrate is allowed to stand for some time, it deposits crystals of the *dihydrate*, $CdCrO_4.2H_2O$. F. J. Malaguti and M. Sarzeau prepared **cadmium tetramminochromate,** $CdCrO_4.4NH_3.3H_2O$, by the method employed for the corresponding zinc salt. By adding alcohol to the acidic soln. of the oxychromate, they obtained a crystalline precipitate of **cadmium pentamminochromate,** $2CdO.3CrO_3.5NH_3.8H_2O$. According to M. Gröger, the ammonium salt, $(NH_4)_2O.4CdO.4CrO_3.3H_2O$, can be regarded as **cadmium hemiamminochromate,** $2CdCrO_4.NH_3.2H_2O$; and when the salt $2(NH_4)_2CrO_4.2CdCrO_4.NH_3.3H_2O$ is allowed to stand in its mother-liquor, for 3 weeks, **cadmium amminochromate,** $CdCrO_4.NH_3.H_2O$, is formed.

F. J. Malaguti and M. Sarzeau prepared **cadmium trioxybischromate,** $3CdO.2CdCrO_4.8H_2O$, by treating a soln. of a cadmium salt with potassium chromate, and boiling the precipitate with oft-removed water until the colour no longer changes. The orange-yellow powder is very slightly soluble in water. C. Freese reported **cadmium oxychromate,** $CdO.CdCrO_4.H_2O$, to be formed from boiling soln. of cadmium sulphate and potassium chromate. Only when a large excess of chromate is present is the product free from acid. C. Freese suggested that the trioxybischromate is really this salt; while B. Skormin obtained a product $4CdO.3CdCrO_4$ with 4·5 to $6{\cdot}0H_2O$. The nature of the product, said M. Gröger, depends on the time of contact of the precipitate with boiling water. Consequently the nature of the basic salts of cadmium chromate is still *sub judice.* B. Skormin described cadmium tetroxytrischromate, $4CdO.3CdCrO_4.nH_2O$. According to F. Rose, the basic chromate has been used as a yellow pigment; but its cost limits it to fine art work.

According to M. Gröger, cadmium chloride and ammonium chromate in aq. soln. interact to form a dark yellow precipitate consisting of microscopic prisms of **ammonium cadmium dihydroxyquadrichromate,** $(NH_4)_2CrO_4.3CdCrO_4.Cd(OH)_2.2H_2O$. The action of hot water on this precipitate is to convert it into a basic cadmium chromate; and when heated, the salt leaves a green residue—possibly cadmium chromite. If 10 c.c. of a soln. of cadmium chloride be dropped into 50 c.c. of a soln. of ammonium chromate, with constant stirring, deep yellow, microscopic prisms are precipitated. The composition corresponds with **ammonium cadmium amminoquadrichromate,** $2(NH_4)_2CrO_4.2CdCrO_4.NH_3.3H_2O$. S. H. C. Briggs obtained **ammonium cadmium diamminochromate,** $(NH_4)_2CrO_4.CdCrO_4.2NH_3$, by dissolving 26 grms. of chromium trioxide and 13 grms. of cadmium oxide in a little water, diluting the soln. to 200 c.c. and adding ammonia so long as the soln. remained clear. The filtrate is allowed to stand for 2 or 3 days. The yellow crystals decompose suddenly when heated to 280°–290°. The **potassium cadmium chromates** resemble the corresponding zinc salts. M. Gröger reported products with the mol. ratios $K_2O : CdO : CrO_3 : H_2O = 1 : 7 : 5 : 3$; $1 : 4 : 4 : 3$; $1 : 3 : 2 : 3$; $1 : 1 : 2 : 2$; and $1 : 1 : 4 : 2$. G. Krüss and O. Unger also prepared the $1 : 1 : 4 : 2$ complex; and B. Skormin, $1 : 7 : 5 : 3$. M. Gröger observed that on mixing aq. soln. of potassium chromate and pure cadmium chloride, a canary-yellow, granular precipitate is formed having the composition $K_2CrO_4.3CdCrO_4.Cd(OH)_2.2H_2O$. Contrary to K. Preis and B. Rayman's statement, this same precipitate is formed by the action of cadmium sulphate and potassium chromate. Cadmium potassium chromate is more stable to boiling water than is zinc potassium chromate; but is finally converted into a lemon-yellow powder, 84·53 per cent. of which is cadmium chromate. On mixing aq. soln. of cadmium chloride and sodium chromate, a yellow, flocculent precipitate is formed which rapidly becomes granular; it is a basic cadmium chromate which easily loses chromic acid when washed with water and absorbs carbon dioxide when exposed to air. When equal vols. of cadmium chloride and sodium chromate soln. are mixed hot and boiled for three days, during which period the precipitate formed is washed twenty-four times, the residue obtained has the mol. proportions $CdO : 0{\cdot}342CrO_3 : 1{\cdot}428H_2O$.

The early workers—L. N. Vauquelin,[16] C. M. Marx, S. M. Godon de St. Menin, etc.—prepared a basic mercurous chromate by treating a soln. of mercurous nitrate with potassium chromate. The presence of nitrous acid prevents the precipitation by reducing chromic acid to chromic oxide. If an excess of nitric acid be present, part of the chromic acid forms mercuric oxide and chromic nitrate and the liquid becomes amethyst-blue, but, on adding more mercurous nitrate, the whole of the chromium is precipitated as mercurous chromate. The same product is obtained whether the soln. be hot or cold, and, added P. and M. M. Richter, statements to the contrary are based on the use of mercurous nitrate contaminated with nitrite. The analyses of L. Gmelin, F. Fichter and G. Oesterheld, and S. M. Godon de St. Menin agree with the assumption that the basic salt—**mercurous oxytrischromate,** $Hg_2O.3Hg_2CrO_4$—is formed. C. Freese, and F. Fichter and G. Oesterheld also obtained it by the hydrolysis of mercurous chromate. The bright red powder turns black when exposed to light; and at a red-heat it is decomposed into chromic oxide, oxygen, and mercury. H. Rose said that it dissolves very sparingly in cold water, but freely in boiling water to form a mercuric salt. A. A. Hayes said that hydrochloric acid converts it into mercurous chloride and chromic acid; ammonia converts it into a black powder which, together with the mercurous oxide, contains about half the chromium as chromic oxide. R. H. Brett said that it is slightly soluble in aq. soln. of ammonium chloride or nitrate. A. A. Hayes added that it is slightly soluble in nitric acid. S. Darby found that basic mercurous chromate is transformed into normal **mercurous chromate,** Hg_2CrO_4, by boiling it with nitric acid; and F. Fichter and G. Oesterheld obtained it by dissolving basic mercurous chromate in boiling $5N$-HNO_3, and cooling; and also by treating a normal soln. of mercurous nitrate with potassium chromate. C. Freese treated an excess of a soln. of mercurous nitrate with potassium dichromate, and washed the product with dil. nitric acid; L. Schulerud added that if twice the proportion of mercurous nitrate be not present, some dichromate is formed. S. Darby found that a complex salt is produced when equimolar parts of potassium dichromate and mercury cyanide are mixed in soln. and enough nitric acid added to the boiling soln. to dissolve the precipitate; on cooling, mercurous chromate is deposited as a crystalline powder. J. A. Atanasiu found that in the electrometric titration of soln. of mercurous nitrate and potassium chromate there is a break corresponding with the formation of mercurous dichromate. Mercurous chromate may form red, rhombic plates, or it may appear as a brown, amorphous precipitate which soon becomes red, and crystalline. F. Fichter and G. Oesterheld said that it should be precipitated from ice-cold soln. since hydrolysis occurs at higher temp., and basic salts are formed. O. D. Swett said that nitric acid is a good solvent for this chromate. According to S. Darby, hydrochloric acid precipitates mercury quantitatively from the soln. of the salt in nitric acid; and ammonia, or potassium hydroxide gives black precipitates. P. and M. M. Richter found that potassium bromide, iodide, and cyanide react similarly; the iodide, for example, precipitates green mercurous iodide which, with more potassium iodide, forms mercury and mercuric iodide, and thus dissolves as $KHgI_3$; with potassium cyanide, the complex $2K_2CrO_4.3HgCy_2$ is formed. F. Fichter and G. Oesterheld said that the salt is less soluble in a soln. of potassium chromate than it is in water. A. Naumann found that the salt is insoluble in acetone; and H. Rose, that it is slightly soluble in dil. nitric acid, very soluble in conc. nitric acid, soluble in a soln. of potassium cyanide, and insoluble in a soln. of mercurous nitrate.

F. Fichter and G. Oesterheld observed that the hydrolysis of normal mercurous chromate furnishes the oxytrischromate (*q.v.*), and subsequently **mercurous oxybischromate,** $Hg_2O.2Hg_2CrO_4$. This salt is formed when freshly precipitated mercurous chromate is boiled with water so long as chromic acid passes into soln. If precipitated mercurous chromate be allowed to stand under the mother-liquid, containing an excess of mercurous nitrate for 7 days, or if it be boiled with mother-liquid for 4 hrs., dark red microscopic needles of the oxybischromate are formed. P. and M. M. Richter obtained **mercurous dioxychromate,** $2Hg_2O.Hg_2CrO_4$, by the action of alkalies on mercurous chromate. This salt forms black crystals, which when dried at a high enough temp. becomes dark green or brownish-black owing to the loss of a little mercury—*vide infra*, oxydimercuriammonium chromate; for the properties of these basic chromates, *vide supra*, mercurous oxytrichromate.

M. Gröger reported **potassium mercurous chromate,** $K_2CrO_4.Hg_2CrO_4$, to be formed by the action of a soln. of mercurous nitrate, containing as little free nitric acid as possible, on a sat. soln. of potassium chromate. After shaking for a couple of weeks, the solid is separated by a suction filter, and dried on a porous tile. The brownish-yellow product decomposes when melted; and when treated with water it furnishes basic mercurous chromate.

According to A. Geuther, and A. J. Cox, if equimolar parts of chromium trioxide and yellow mercuric oxide be boiled with water, red crystals of **mercuric chromate,** $HgCrO_4$, are formed. The dark garnet-red, rhombic prisms become still darker when heated, but they lose no weight at 135°; at a red-heat, the salt decomposes yielding mercury, oxygen, and chromic oxide. The salt is hydrolyzed by cold water, and with hot water, a residue $7HgO.2CrO_3$ is formed; the hydrolysis can proceed further until finally mercuric oxide remains. If the conc. of the chromic acid be less than 0·46 mol CrO_3 per litre, the normal chromate is unstable—Fig. 50. Cold conc. nitric acid transforms the salt into $7HgO.2CrO_3$; moderately conc. nitric and sulphuric acids also form $7HgO.2CrO_3$. The salt is completely soluble in hydrochloric acid, and from this soln., alkali-lye precipitates mercuric oxide. M. Gröger obtained **mercuric diamminochromate,** $HgCrO_4.2NH_3.H_2O$, by dropping a soln. of 8·64 grms. of mercuric oxide in 6 c.c. of nitric acid of sp. gr. 1·41, and diluted to 20 c.c. into 50 c.c. of a soln. of 2 mols. of ammonium chromate. A. Naumann said that the mercuric chromate is insoluble in ethyl acetate and in acetone.

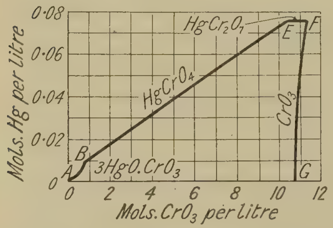


Fig. 50.—Conditions of Equilibrium of Mercuric Chromates at 25°.

A. J. Cox studied the ternary system: $HgO–CrO_3–H_2O$ at 25°, and found that under these conditions only one basic salt is formed. The invariant points, *A*, *B*, *E*, *F*, *G*, Fig. 50, are indicated in Table IV. where concentrations are expressed

TABLE IV.—INVARIANT POINTS IN THE SYSTEM $HgO–CrO_3–H_2O$ AT 25°.

Mols CrO_3.	Mols Hg.	Solid phases.	Fig.
—	—	$HgO+3HgO.CrO_3$	*A*
0·456	0·035	$3HgO.CrO_3+HgCrO_4$	*B*
10·46	0·758	$HgCrO_4+Hg_2Cr_2O_7$	*E*
11·11	—	$Hg_2Cr_2O_7+CrO_3$	*F*
10·8	—	CrO_3	*G*

in mols per litre. The results are also shown graphically in Fig. 50. It was also found that at 50°

CrO_3 .	0·00013	0·0047	0·705	0·499	0·620	0·740	1·006
Hg . .	small	0·00015	0·0745	0·049	0·066	0·072	0·1
	HgO	$3HgO.CrO_3$		labile		stable	
				$HgCrO_4$			

N. A. E. Millon boiled yellow mercuric oxide with a soln. of potassium dichromate and obtained **mercuric dioxychromate,** $2HgO.HgCrO_4$, or $3HgO.CrO_3$. B. Skormin obtained the same product from freshly precipitated yellow mercuric oxide and an excess of a soln. of potassium dichromate. N. A. E. Millon, B. Skormin, C. Freese, and A. J. Cox also obtained it by treating a soln. of mercuric nitrate with potassium dichromate or chromate. The conditions of equilibrium are illustrated by Fig. 51. N. A. E. Millon found that the same product is obtained with mercuric chloride, but A. Caillot could not prepare it with mercuric bromide. A. J. Cox, and A. Geuther obtained it by the hydrolysis of mercuric chromate; and A. Geuther, by pouring a cold solution of mercuric carbonate in conc. nitric acid into cold water—the precipitate is at first yellow, but soon becomes scarlet-red. B. Skormin also prepared this salt. A. J. Cox showed that the minimum conc. of acid in which the salt is stable is 0·00026N-HNO_3 at 50°. J. L. Gay Lussac and L. J. Thénard found that mercuric chromate is decomposed with incandescence when heated with potassium.

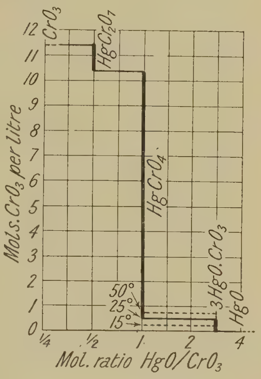


FIG. 51. — Conditions of Equilibrium in the System: $HgO–CrO_3–H_2O$ at 25°.

Several other basic salts have been reported; thus, E. Jäger and G. Krüss, and F. W. Clarke and D. Stern reported $6HgO.CrO_3$, but neither B. Skormin, nor A. J. Cox could verify its existence; E. Jäger and G. Krüss also reported $5HgO.CrO_3$, but A. J. Cox could not confirm the result; N. A. E. Millon, and F. W. Clarke and D. Stern, $4HgO.CrO_3$, but neither A. J. Cox, nor B. Skormin could accept the evidence; M. Gröger stated that this compound forms the ammino compound $3(4HgO.CrO_3).2NH_3.3H_2O$, by extraction with a soln. of ammonium chromate. A. Geuther, and F. W. Clarke and D. Stern reported $7HgO.2CrO_3$, but C. Freese, B. Skormin, and A. J. Cox were unable to verify the result; and A. Geuther reported $2HgO.CrO_3$, but A. J. Cox could not confirm the result. F. Rose mentioned the use of the basic chromates as pigments—*purple red,* or *chrome red.*

F. M. Litterscheid added ammonia to a soln. of potassium dichromate, mixed with an excess of mercuric chloride, in the cold until the liquid had an alkaline reaction; and obtained **dimercuriammonium chromate,** $(NHg_2)_2CrO_4.2H_2O$. The same product was obtained by adding an excess of ammonia to a cold soln. of mercuric chloride, and then adding a soln. of potassium chromate or dichromate. The lemon-yellow precipitate gave off no water when heated for many hours at 100°; it is virtually insoluble in water, and in a cold 10 per cent. soln. of ammonia—free from ammonium salts. The moist salt dissolves in soln. of ammonium salts.

The moist compound is freely soluble in 10 per cent. hydrochloric acid, but if the salt has been dried it dissolves with difficulty. The dried salt is easily soluble in 25 per cent. hydrochloric acid; and is insoluble in boiling, conc. nitric or sulphuric acid, with gradual decomposition; the moist salt is more easily attacked by these acids. F. W. Clarke and D. Stern obtained what they regarded as a complex salt, *ammonium dimercuriammonium chromate.* According to E. C. Franklin, a salt of this composition can be regarded as *mercuric hydroxyimidochromate,* $(HO.Hg.NH.Hg)_2CrO_4$; or as *oxydimercuriammonium chromate,* $(NH_2.Hg.O.Hg)_2CrO_4$. F. Fichter and G. Oesterheld obtained it by the action of aq. ammonia on mercurous chromate, and said that P. and M. M. Richter were wrong in saying that the product of the action is mercurous dioxychromate; the action of alkalies furnishes a mixture of mercurous oxide, or mercuric oxide and mercury. C. Hensgen obtained this product by the action of a hot, conc. soln. of ammonium chromate on mercuric chloride, and by boiling the complex dichromate with aq. ammonia or potash-lye; C. H. Hirzel, by digesting basic oxydimercuriammonium chromate (*vide infra*) with aq. ammonia, and washing with hot water; and B. Skormin, by mixing an excess of a cold, conc. soln. of ammonium chromate with mercuric nitrate, and boiling the orange-yellow, amorphous precipitate with water until it gives no reaction for nitric acid, and is colourless. The yellow product can be represented as an amidochromate, $3HgO.Hg(NH_2)_2CrO_3$; it becomes greyish-yellow at 100°, and begins to decompose into ammonia and a basic *mercuric amidochromate,* $3HgO.Hg(NH_2)_2CrO_3$. When heated in a tube, it gives a yellowish-red sublimate and mercury; it glows brightly with sparking when heated in air; it is not decomposed by potash-lye, but with a boiled soln. ammonia is evolved; it develops ammonia when heated with a soln. of potassium iodide; and it is soluble in hydrochloric acid, but nitric and sulphuric acids have scarcely any action.

C. H. Hirzel prepared **oxydimercuriammonium mercuric oxyquadrichromate,** $HgO.3HgCrO_4(NH_2.Hg.O.Hg)_2CrO_4$. He said that a cold soln. of ammonium dichromate has no apparent action on yellow mercuric oxide; but when the mixture is boiled this salt is formed as an orange-yellow, sandy powder. C. Hensgen regarded it as a mixture of mercuric oxide or basic mercuric chromate, and ammonium oxydimercuriammonium dichromate; and E. C. Franklin represented it by the formula $3HgCrO_4.HgO.(HO.Hg.NH.Hg)_2CrO_4$. C. H. Hirzel found that when heated in a tube, the compound darkens in colour and then decomposes with a feeble detonation; or it may yield nitrous vapours, a yellow sublimate of mercury, and chromic oxide. Ammonia transforms it into lemon-yellow oxydimercuriammonium chromate; potash-lye makes the colour paler, but gives no ammonia; boiling soln. of potassium iodide or sulphide liberate the nitrogen quantitatively as ammonia; conc. nitric acid decomposes it without its passing into soln.; and it forms a reddish-yellow soln. with hydrochloric acid.

S. Löwenthal described *mercuric amidochromate,* $Hg_3NH_2(CrO_4)_2$; and M. Gröger said that *potassium mercuric chromate* is not produced by treating mercuric nitrate or chloride as in the analogous process for the mercurous salt, but rather yields a basic chromate which adsorbs potassium chromate.

A. J. Fairrie,[17] and C. W. Eliot and F. H. Storer treated a soln. of potash-alum with potassium chromate, and obtained a precipitate which after pressing, corresponded with **aluminium dioxychromate,** $Al_2O_2.CrO_4.nH_2O$. M. Siewert, and A. Maus also dissolved aluminium hydroxide in a soln. of chromic acid, and on evaporating the liquid, obtained aluminium hydroxide, and an acidic soln. E. Fleischer observed that no precipitate is produced by adding potassium dichromate to a soln. of potash-alum; and when the liquid is evaporated alum first crystallizes out, and then potassium dichromate. There is here no satisfactory evidence of the formation of an aluminium chromate. L. Blanc, however, regarded the formation of the basic chromate as proved. According to M. Gröger, the addition of aq. potassium chromate to a soln. of potassium-alum precipitates basic aluminium sulphates; as the quantity of the chromate is increased, the precipitate becomes mixed with an increasing amount of chromate; when the alum and potassium chromate are in the ratio $Al_2O_3 : 2CrO_3$, no precipitate is formed. On mixing soln. of aluminium chloride and potassium chromate, a yellow precipitate is formed which has the composition $2Al_2O_3.CrO_3.6H_2O$; the precipitation of the aluminium is not complete until 3 mols of potassium chromate have been added for each mol of aluminium chloride. Soln. made by dissolving aluminium hydroxide in chromic acid always contain Al_2O_3 and CrO_3 in the proportion of 1 : 1·4 to 1·45; from this soln., the insoluble basic chromate mentioned above separates on keeping. No indication was observed of the formation of the compound $Al_2O_3.CrO_3.7H_2O$, described by A. J. Fairrie. N. A. Orloff said that aluminium chromate, like beryllium chromate, is hydrolyzed by water without forming any definite basic salt; and L. Petrik represented the reaction: $Al_2(SO_4)_3+3K_2CrO_4+3H_2O=Al_2(OH)_6+3CrO_3+3H_2SO_4$—*vide supra,* the colour of chromic oxide. S. H. C. Briggs added a soln. of 4 grms. of hydrated aluminium chloride in 25 c.c. of water to a soln. of 15 grms. of sodium chromate in 30 c.c. of water, and heated the mixture for an hour on the water-bath. The filtered precipitate was washed with a little water, and dried in vacuo. A mixture of 2 grms. of chromic trioxide, 2 c.c. of water, and 1·8 grms. of the powdered product was heated in a sealed tube at 200° to 210° for 4 hrs., and the crystalline, insoluble, lemon-yellow product corresponded with **aluminium oxydichromate,** $3Al_2O_3.2CrO_3.6H_2O$, or $Al_2O_3.2(AlO)_2CrO_4.6H_2O$.

According to R. E. Meyer,[18] and C. Winkler, a soln. of a neutral salt of indium gives an insoluble precipitate of an **indium chromate** when treated with an alkali chromate. A soln. of indium sesquioxide in aq. chromic acid, does not crystallize when evaporated, or when allowed to stand in a desiccator. Only a viscid syrup is produced. W. Crookes[19] observed that **thallous chromate,** Tl_2CrO_4, is precipitated when a soln. of a neutral thallous salt is treated with potassium chromate; and also by digesting thallous dichromate with ammonia. E. Carstanjen obtained it from a soln. of thallous carbonate in aq. chromic acid. G. Canneri observed that M. Gröger's method for basic lead chromates yields with thallous salts, only the normal chromate. The action of dil. acid on thallous chromate yields thallous dichromate, but if a quantity of sulphuric acid insufficient to dissolve the chromate is employed and the boiling soln. is filtered and conc. **thallous hydrochromate,** $TlHCrO_4.Tl_2CrO_4$, in cinnabar-red crystals, and often in cruciform twins, is formed. Thallous chromate darkens when heated, and then melts without decomposition. At a higher temp. the salt decomposes. J. W. Retgers said that the crystals are probably not isomorphous with potassium chromate or thallous sulphate. According to G. Canneri, the e.m.f. of the electrode, mercury amalgam against a saturated thallous chromate soln. varies continuously with the temp., the curve exhibiting no characteristic point corresponding with the change in colour which thallous chromate crystals undergo when heated at 60°. Similarly the conductivity of sat. thallous chromate shows no sudden variation between 25° and 90°. The pale yellow or lemon-yellow amorphous precipitate is slightly soluble in water. E. Rupp and M. Zimmer said that 100 parts of water at 60° dissolve 0·03 part of thallous chromate; and P. E. Browning and G. P. Hutchins said that 100 grms. of water at 100° dissolve 0·2 grm. E. Carstanjen observed that it is attacked by dil. hydrochloric acid; and W. Crookes found that it is dissolved by moderately conc. boiling hydrochloric acid, and on cooling vermilion-red crystals separate—probably the trichromate. E. Carstanjen added that with conc. hydrochloric acid, thallous chloride is separated, and a green soln. is formed. W. Crookes also observed the formation of thallium chloride by the action of conc. hydrochloric acid. E. Carstanjen found that dil. sulphuric acid attacks thallous chromate slowly in the cold, and when the acid is heated, E. Willm said that the di- or tri-chromate is formed. With conc. sulphuric acid, violet thallium chrome-alum separates out. E. Carstanjen observed that dil. nitric acid, as well as conc. acetic acid, do not dissolve thallous chromate in the cold, but with boiling soln., a little chromate is dissolved. It also behaves similarly towards aq. soln. of ammonia and sodium carbonate. M. Lachaud and C. Lepierre found that a litre of boiling N-KOH dissolves 3·5 grms. of thallous chromate, and on cooling, almost all separates out in six-sided pyramidal crystals. A soln. of potash-lye of sp. gr. 1·3 dissolves 18 grms. of chromate per litre. Molten potassium hydroxide converts it into thallic oxide. When thallous and potassium chromates are melted with potassium nitrate, **potassium thallous chromate,** $KTlCrO_4$, or $K_2CrO_4.Tl_2CrO_4$, is formed. M. Hebberling, and W. Strecker observed that reddish-yellow or brown precipitates are obtained when soln. of thallic salts are treated with soluble chromates or dichromates. The result is **thallic chromate.** According to G. Canneri, thallic chromate may be obtained pure as a golden yellow, crystalline powder by dissolving freshly-precipitated thallic oxide in excess of chromic anhydride soln. According to L. F. Hawley, **potassium thallic chromate,** $KTl(CrO_4)_2.2H_2O$, is obtained by adding potassium hydroxide to a soln. of thallic hydroxide in chromic acid. The yellow salt is rapidly hydrolyzed by water unless a large excess of chromic acid is present.

L. Haber[20] observed no precipitation occurs when cerium, lanthanum, and didymium salts are boiled with chromic acid, or with potassium or sodium dichromate, but a basic salt is precipitated when thorium or zirconium salts are similarly treated. J. F. John, and A. Beringer found that a soln. of cerous carbonate in aq. chromic acid slowly deposits **cerous chromate** as a yellow powder, and when the mother-liquor is evaporated, crystals of an acid salt are formed. According to S. Jolin, soln. of cerous salts also give precipitates of basic cerous chromates when treated with soln. of potassium chromate or dichromate. F. Zambonini and G. Carobbi found that when an intimate mixture of cerous chloride and potassium chromate is heated to 1000°, chromic oxide and cerium dioxide are formed. M. M. Pattison and J. Clarke found that when the chromates obtained by evaporating to dryness a soln. of the mixed oxides of cerium, didymium, and lanthanum in chromic acid, are heated to about 110°, only the cerium chromate is decomposed to form an insoluble powder, while the chromates of didymium and lanthanum remain unchanged. A. Brauell, and L. M. Dennis and B. Dales founded analytical processes on this reaction; G. Krüss and A. Loose, and W. Muthmann and C. R. Böhm found that the fractional precipitation by potassium chromate of the ceria earths proceeds in the order: La, Pr, Nd, Sm; and of the yttria earths, in the order: Tb, Yb, Er, Y, Gd. Processes of separation have been devised—by J. E. Egan and C. W. Balke, B. S. Hopkins and C. W. Balke, H. Moissan and A. Étard, C. R. Böhm, W. Muthmann and C. R. Böhm, L. M. Dennis and B. Dales, R. J. Meyer and J. Wuorinen, H. C. Holden and C. James, and C. James—based on this reaction—*vide* **5**. 38, 6. According to F. Frerichs and F. Smith, a soln. of lanthanum sulphate and potassium chromate gives a precipitate consisting of **lanthanum chromate,** $La_2(CrO_4)_3.8H_2O$. Lanthanum chromate is very liable to form a sparingly soluble potassium complex salt so that P. T. Cleve said that the precipitate probably contains the complex salt. The precipitate is yellow, granular, and consists of microscopic crystals. It is sparingly soluble in cold water and freely soluble in acids. P. T. Cleve obtained the octohydrate by treating a soln. of lanthanum nitrate with potassium chromate. H. T. S. Britton also prepared the *octohydrate* of lanthanum chromate by dissolving about 2 grms. of the rare earth in the minimum amount of chromic acid soln.; diluting the liquid to 2 litres; and gradually adding $0{\cdot}1M$-K_2CrO_4. When the amount of chromic acid used was kept sufficiently low, the quantity of potassium chromate required was small, thereby causing the simple chromate alone to be precipitated, but if too great a quantity of acid had been employed a correspondingly large amount of precipitant was necessary, and this often caused the precipitation of double chromates together with varying amounts of simple chromates. The salt is a bright yellow mass of microscopic, prismatic needles. 100 grms. of water at 25° dissolve 0·020 grm. calculated as anhydrous salt. The solubility is less at higher temp. F. Zambonini and G. Carobbi obtained the anhydrous salt by heating the rare earth chloride and potassium chromate over 600°; and they obtained the *monohydrate*, $La_2(CrO_4)_3.H_2O$, by precipitation from cold soln. G. Carobbi studied the system $La_2(CrO_4)_3$–$(NH_4)_2CrO_4$–H_2O at 25°—Fig. 52. The only complex salt formed was **ammonium lanthanum hexachromate,** $La_2(CrO_4)_3.3(NH_4)_2CrO_4.5H_2O$. The study of the system is complicated by the alteration of ammonium chromate into dichromate, so that when the ammonium chromate is in excess, ammonium dichromate crystallizes out, and when lanthanum chromate is in excess, the salt $La_2(CrO_4)_3.8H_2O$ separates. H. T. S. Britton obtained **potassium lanthanum tetrachromate,** $K_2CrO_4.La_2(CrO_4)_3.6H_2O$, as indicated above. P. T. Cleve found that if an excess of potassium chromate be employed, there is formed **potassium lanthanum heptachromate,** $4K_2CrO_4.La_2(CrO_4)_3.nH_2O$. G. Carobbi studied the system $La_2(CrO_4)_3$–K_2CrO_4–H_2O at 25°, and found that the existence of the hydrated complex chromates, 1 : 1 : 2; 1 : 3 : 2; 1 : 4 : 2; 1·4 : 5 : 2; and 1 : 5 : 2, are indicated on the isothermal curve, Fig. 53. F. Frerichs and F. Smith obtained a precipitate resembling that with the lanthanum salt when a soln. of a didymium salt is treated with potassium chromate. The precipitated **didymium chromate,** $Di_2(CrO_4)_3.8H_2O$, was said by P. T. Cleve to be contaminated with a complex potassium salt which is obtained by treating a soln. of didymium nitrate with an excess of potassium chromate. H. T. S. Britton also obtained the bright yellow *octohydrate* of **praseodymium chromate,** $Pr_2(CrO_4)_3.8H_2O$, as in the case of the lanthanum salt; 100 grms. of water at 25° dissolve the eq. of 0·021 grm. of the anhydrous salt. F. Zambonini also prepared the anhydrous salt, as well as the *decahydrate*, $Pr_2(CrO_4)_3.10H_2O$, by the methods indicated in connection with the anhydrous, and the monohydrated lanthanum salts. H. T. S. Britton likewise prepared the dull yellow *octohydrate* of **neodymium chromate,** $Nd_2(CrO_4)_3.8H_2O$, with a solubility of 0·027 grm. per 100 grms. of water at 25°. E. Baur said that this salt is olive-brown; and N. A. Orloff, moss-green. As in the case of the praseodymium salt, F. Zambonini and G. Carobbi also prepared the anhydrous salt, and the decahydrate. By adding an excess of potassium chromate to the soln. of a didymium salt, P. T. Cleve obtained yellow **potassium didymium chromate,** $K_2CrO_4.Di_2(CrO_4)_3.nH_2O$. It is hydrolyzed when washed with water with the loss of potassium chromate. H. T. S. Britton obtained a mixture of a basic chromate and **potassium praseodymium chromate** by adding an excess of potassium chromate to a chromic acid soln. of praseodymia; and similarly with **potassium neodymium chromate.** H. T. S. Britton obtained the *octohydrate* of **samarium chromate,** $Sa_2(CrO_4)_3.8H_2O$, as in the case of the lanthanum salt; 100 grms. of water at 25° dissolved 0·043 grm. of the salt calculated as anhydrous. F. Zambonini and G. Carobbi prepared the anhydrous salt and the *enneahydrate*, $Sa_2(CrO_4)_3.9H_2O$, as in the case of the anhydrous and monohydrated lanthanum salts. By adding potassium chromate to a soln. of a samarium salt, P. T. Cleve obtained a yellow, crystalline precipitate of **potassium samarium chromate,** $K_2CrO_4.Sa_2(CrO_3)_3.6H_2O$. No precipitation occurs with potassium dichromate. H. T. S. Britton found that

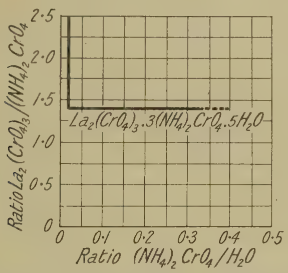


FIG. 52.—Equilibrium in the System: $La_2(CrO_4)_3$–$(NH_4)_2CrO_4$–H_2O at 25°.

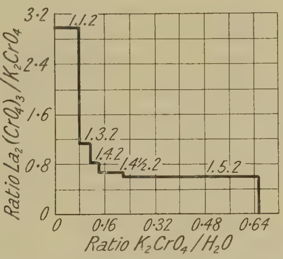


FIG. 53.—Equilibrium in the System: $La_2(CrO_4)_3$–K_2CrO_4–H_2O at 25°.

with an excess of potassium chromate the composition of the yellow flocculent precipitate varied with the composition of the precipitant; a complex salt is probably formed. The application of the phase rule is required to establish the nature of the complex salts. In general, the addition of a soln. of potassium chromate to an aq. salt soln. causes the precipitation of (*a*) in the case of lanthanum, the simple chromate if the excess of precipitant is small, (*b*) praseodymium, the simple chromate, (*c*) neodymium, a mixture of simple and basic chromates, (*d*) samarium, a basic chromate of indefinite composition. H. T. S. Britton continued: The only normal chromates which have been found hitherto belong to the cerite-group, the bases of which are believed to be among the strongest of the rare earths. Even among the members of this group there is a gradually increasing tendency to form basic chromates in the case of the weaker bases, neodymia and samaria.

G. Krüss and A. Loose, and W. Muthmann and C. R. Böhm obtained precipitates of **terbium chromate,** and of **gadolinium chromate** by adding potassium chromate to soln. of the corresponding salts. P. B. Sarder obtained the complex **potassium gadolinium chromates,** $K_2CrO_4.Gd_2(CrO_4)_3.7H_2O$, and $5K_2CrO_4.2Gd_2(CrO_4)_3.10H_2O$. G. Jantsch and A Ohl prepared **dysprosium chromate,** $Dy_2(CrO_4)_3.10H_2O$, as a sparingly soluble precipitate, by the interaction of soln. of the nitrate and of potassium chromate. The greenish-yellow, crystalline powder is soluble in water—at 25°, 100 c.c. of the soln. contain 1·0002 grms. of salt. When heated to 150°, the chromate loses 3·5 mols. of water; and at 150°, it decomposes. N. J. Berlin said that a basic yttrium chromate is formed when a soln. of chromic acid is sat. with yttria. The brown soln. deposits a brown powder. The salt was also obtained by O. Popp, G. Krüss and A. Loose, and W. Muthmann and C. R. Böhm. J. F. John observed that a soln. of yttrium carbonate in aq. chromic acid deposits orange-yellow crystals, of **yttrium chromate,** $Y_2(CrO_4)_3.nH_2O$, easily soluble in water. N. J. Berlin said that the spontaneous evaporation of the soln. gives yellowish-brown deliquescent crystals. P. T. Cleve obtained **potassium yttrium chromate,** $K_2CrO_4.Y_2(CrO_4)_3.nH_2O$, as a yellow, crystalline powder, by the action of potassium dichromate on yttrium carbonate. G. Krüss and A. Loose, and W. Muthmann and C. R. Böhm also prepared **erbium chromate,** and **ytterbium chromate.**

According to S. M. Godon de St. Menin,[21] when an aq. soln. of chromic acid mixed with hydrated silicic acid is evaporated, a reddish-yellow powder—silicon chromate—is formed, insoluble in water, and is not decomposed at an elevated temp. It is highly probable that no compound is formed. G. A. Quesneville, however, said that very little silicic acid is taken up by the soln., and that all the chromic acid is removed by washing. M. Blondel found that a conc. aq. soln. of chromic acid dissolves titanic acid in amounts depending on the conc., and temp. of the soln., and on the previous history of the titanic acid. When a conc. soln. containing one part of titanic oxide and 4 parts of chromium trioxide is diluted with 8 parts of water at 50° or 6 parts of water at 100°, **titanium tetroxychromate,** $3TiO_2.2CrO_3.H_2O$, or $TiO_2.2(TiO)CrO_4.H_2O$, is precipitated; with 25 parts of cold water, or 8 parts of water at 100°, **titanium trioxychromate,** $TiO_2.(TiO)CrO_4.2H_2O$, is produced; while with 50 parts of cold water or 12 parts of water at 100°, **titanium pentoxychromate,** $2TiO_2.(TiO)CrO_4.3H_2O$, is formed. On adding an eq. of ammonia to the same conc. soln. of the two oxides, $TiO_2.(TiO)CrO_4.2H_2O$ is precipitated, and the evaporation of the mother-liquor in vacuo yields hexagonal prisms of **ammonium titanium chromate,** $(NH_4)_2CrO_4.Ti(CrO_4)_2.H_2O$. All this has not yet been verified. M. Weibull found that **zirconium chromate** is precipitated when a zirconium salt soln. is treated with chromic acid or a dichromate. The flocculent, orange-red precipitate is sparingly soluble in dil. acids; and when washed with water chromic acid passes into soln. L. Haber said that the composition of the precipitate is indefinite. F. P. Venable and L. V. Giles, however, said that a definite salt $2ZrO(OH)_2.ZrOCrO_4.8H_2O$, **zirconyl tetrahydroxychromate,** is produced as a granular, yellow precipitate by dissolving zirconium hydroxide in a boiling soln. of chromic acid, diluting, and again boiling the soln. The compound obtained loses a considerable quantity of its water at 110°, but the whole of it is lost only at 200°. It is suggested that its formation occurs as follows: first, normal zirconium chromate is formed, which is immediately hydrolyzed to $ZrOCrO_4$; some of the zirconium hydroxide is partly dehydrated to give $ZrO(OH)_2$. These two substances then combine to give the yellow insoluble basic salt. According to P. Krishnamurti and B. B. Dey, the addition of a large excess of a sat. soln. of potassium dichromate to a conc. soln. of zirconium oxychloride precipitates **zirconium octohydroxychromate,** $Zr_3(OH)_8(CrO_4)_2$; with a dil. soln. of the zirconium salt, **zirconium hexahydroxychromate,** $Zr_2(OH)_6CrO_4$, is formed; and with very dil., boiling soln. of the oxychloride, and only a slight excess of dichromate, the product washed with boiling water corresponds with **zirconium decahydroxychromate,** $Zr_3(OH)_{10}CrO_4$. S. H. C. Briggs added a soln. of 7 grms. of crystalline zirconium nitrate in 50 c.c. of water to 10 grms. of potassium dichromate in 80 c.c. of water, after a day, the precipitate was filtered off, washed with a little water, and dried in vacuo, 2·5 grms. of the dried powder was heated in a sealed tube at 190° for 3½ hrs. with 6 grms. chromic trioxide, and 6 c.c. of water. The orange-red, homogeneous, insoluble, crystalline powder had the composition of **zirconium hexacosioxypentachromate,** $9ZrO_2.5CrO_3.12H_2O$, or $13ZrO_2.5Zr(CrO_4)_2.24H_2O$.

W. Muthmann and E. Baur[22] found that if a soln. of potassium chromate is dropped carefully into a boiling soln. of commercial thorium nitrate, first thorium will be precipitated completely as chromate and afterwards some rare earths begin to appear, indicated by a change in colour of the precipitate. This is the principle of E. Baur's method of separating the rare earths—*vide supra.* C. Palmer obtained **thorium chromate,** $Th(CrO_4)_2.H_2O$, by allowing a soln. of freshly precipitated thorium hydroxide in aq. chromic acid to stand for some time, or by mixing boiling soln. of a mol of thorium nitrate and 2 mols of potassium dichromate. The *monohydrate* appears as an orange-red, crystalline powder. He also prepared the *trihydrate* by evaporating in vacuo a soln. of freshly precipitated thorium hydroxide in a cold soln. of chromic acid. L. Haber prepared it as an orange-yellow, crystalline powder by boiling thorium nitrate for some time with aq. chromic acid, or better with sodium or potassium dichromate. Under similar conditions no precipitate is formed with cerium, lanthanum, or didymium salts. J. J. Berzelius said that the precipitated thorium chromate dissolves in an excess of chromic acid. The orange-yellow, rhombic plates lose their water of crystallization at 180°; and they dissolve in moderately conc. mineral acids. J. Chydenius obtained yellow crystals of the *octohydrate* by evaporating over sulphuric acid a soln. of thorium hydroxide in aq. chromic acid, or an aq. soln. of thorium chloride and chromic acid. The salt loses its combined water at 100°, and the aq. soln. does not become turbid when boiled. C. Palmer also obtained **thorium dihydroxychromate,** $Th(OH)_2CrO_4$, by mixing a soln. of a mol of thorium nitrate and one of 3 mols of potassium chromate; the precipitate first formed dissolves. The soln. furnishes golden-yellow crystals of the basic salt. According to H. T. S. Britton, if thorium hydroxide is suspended in a dil. soln. of chromic acid, it will be converted gradually into the normal chromate, the change occurring more rapidly on boiling. No basic salt of definite composition has been found. The composition varies, gradually approaching that of the normal chromate, but the conversion is complete only after long boiling. Crystals may appear to be slightly basic owing to the adsorption of normal chromate. The so-called basic thorium chromates are really mixtures of thorium hydroxide and thorium chromate. In other words, these basic chromates may be regarded as so-called adsorption compounds, or, taking into account the slight solubility of the normal thorium chromate, as having been produced by the simultaneous precipitation of both the hydroxide and the chromate. The basic chromate of C. Palmer is a special case of such a mixture. When soln. of thorium salts, to which potassium chromate has been added in quantities insufficient to give a permanent precipitate owing to the acid liberated by hydrolysis, are allowed to stand at room temp., if the conc. is sufficiently great, crystals of thorium chromate trihydrate will be deposited slowly; but deposition occurs almost immediately from the boiling soln. The solubility of thorium chromate in soln. of chromic acid at 25°, when the composition is represented in percentages by weight, is as follows:

CrO_3 .	0·033	13·09	39·49	40·23	52·60	61·38	61·84	62·78
ThO_2 .	0·044	6·52	24·22	23·04	7·91	17·65	6·27	0
	$Th(CrO_4)_2.3H_2O$			$Th(CrO_4)_2.CrO_3.3H_2O$			CrO_3	

The results are plotted in Fig. 54. The compound **thorium chromatobischromate,** $Th(CrO_4)_2.CrO_3.3H_2O$, is better represented by this formula than by $Th(Cr_2O_7)(CrO_4).3H_2O$, because it can exist in equilibrium only with highly conc. soln. of chromic acid. It is decomposed by water.

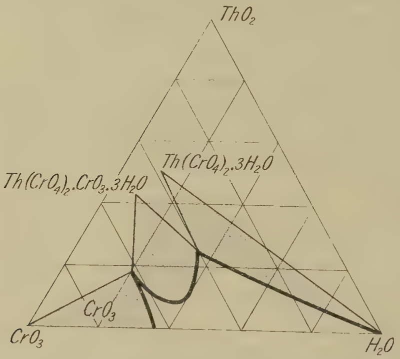


Fig. 54.—Equilibrium Diagram of the System: ThO_2–CrO_3–H_2O at 25°.

According to J. J. Berzelius,[23] when stannous chloride is added to an excess of a soln. of potassium chromate, and the liquid agitated, yellow, curdy flocks of **stannous chromate** are precipitated; but if to a soln. of stannous chloride a dil. soln. of potassium chromate be added in small portions at a time, with constant agitation, a greenish precipitate of *chromic stannate* is formed. If the soln. of the tin-salt contains free acid, no precipitate is formed, and the soln. is green. P. Grouvelle obtained a similar result. According to J. J. Berzelius, stannic chloride soln., not containing free acid, gives a yellow precipitate of **stannic chromate,** when treated with potassium chromate. The supernatant liquor acquires an orange-yellow colour in consequence of the liberation of chromic acid. The dried precipitate is brownish-yellow, and when ignited forms violet *chromic stannate.* T. Leykauf said that if stannic chromate be heated to bright redness, a violet mass is obtained which communicates to pottery glazes colours ranging from rose-red to violet. F. J. Malaguti studied the *minéral lac,* or *laque minérale,* obtained by igniting 50 parts of stannic oxide with one part of chromic oxide. The pink or crimson colour develops more easily if calcium carbonate is a constituent of the ignited mixture. This is essentially the *chrome-tin pink* pottery colour. The pink coloration is probably the colour of highly dispersed chromic oxide, and the stannic oxide acts as a mordant. Other inert oxides can be used, but stannic oxide resists attack by the pottery glaze—*vide supra,* chromic oxide. This subject was studied by H. Stein, G. Steinbrecht, C. Lauth and G. Dutailly, H. A. Seyer, A. S. Watts, R. C. Purdy and co-workers, F. Rhead, W. A. Hall, and W. A. Lethbridge.

The mineral described by M. W. Lomonosoff,[24] J. G. Lehmann, and P. S. Pallas as *nora minera plumbi;* by J. G. Wallerius, as *minera plumbi rubra;* by A. G. Werner, as *Rothes Bleierz;* and L. C. H. Macquart, as *plomb rouge,* was found by L. N. Vauquelin, in 1757, to contain a new element in the form of chromate so that R. J. Haüy called it *plomb chromaté.* J. F. L. Hausmann proposed the name *kallochrom;* W. H. Miller, *lehmannite;* F. S. Beudant, *crocoise*—from κρόκος, saffron; F. von Kobell, *crocoisite;* and A. Breithaupt, **crocoite** (*Krokoit*), which was afterwards adopted by F. von Kobell and others. Analyses of the mineral by C. H. Pfaff,[25] J. J. Berzelius, C. Bärwald, and A. Liversidge; and of artificial preparations by J. J. Berzelius, H. Golblum and G. Stoffella, M. Gröger, A. J. Cox, N. S. Manross, L. Bourgeois, M. Lachaud and C. Lepierre, and C. Lüdeking, agree that the product is **lead chromate,** $PbCrO_4$.

L. N. Vauquelin, and J. J. Berzelius obtained normal lead chromate by precipitation from a soln. of lead nitrate or acetate by the addition of potassium chromate or dichromate. The precipitate is yellow, and, according to E. F. Anthon, the colour is paler when precipitated from cold soln. than from hot soln., since the former is more or less hydrated; while L. N. Vauquelin said that a trace of potassium chromate in the precipitate darkens the colour. C. O. Weber, and M. Dullo discussed the effect of an excess of lead—*vide infra*. L. Dede and P. Bonin said that the precipitation is incomplete in acetic acid soln. if much chloride be present. Z. Karaoglanoff and B. Sagortscheff found that with lead chloride as the soluble lead salt, some $Pb_2Cl_2(CrO_4)$ is formed. The above mode of preparation, using the potassium or sodium chromates or chromic acid as precipitants, and soln. of varying degrees of concentration, were used by T. Gobel, F. G. Kidd, P. Jannasch, H. Golblum and G. Stoffella, J. Milbauer and K. Kohn, M. Fraudel, J. G. Gentele, E. Guignet, F. Rose, A. J. Cox, F. Auerbach and H. Pick, O. Meyer, M. Gröger, P. Breteau and P. Fleury, A. de Schulten, and G. Zerr and G. Rübencamp. J. Massignon and E. Watel obtained lead chromate by the action of soln. of lead salts on calcium chromate. G. N. Ridley showed that the precipitate formed on mixing aq. soln. of lead acetate and potassium dichromate is finer grained when the soln. are more dilute; but temp. has little influence on the fineness of grain. Precipitated lead chromate is amorphous. M. Lachaud and C. Lepierre found that the amorphous chromate is readily crystallized by boiling, say, 5 grms. with a soln. of 20 grms. of chromic acid in 70 grms. of water; L. Bourgeois boiled the precipitated chromate with dil. nitric acid (1 : 5 or 6), filtered the hot decanted liquid through glass-wool, and allowed it to cool slowly; he also obtained well-defined crystals by heating the chromate in a sealed tube at 150°. C. Lüdeking, and G. Cesaro allowed a soln. of lead chromate in potash-lye to stand exposed to the air. G. N. Ridley found that in alcoholic soln., precipitation is slow; and that the addition of an alcoholic soln. of potassium dichromate to a glycerol soln. of lead acetate produces only a slight turbidity—but precipitation occurs when water is added. No precipitation occurs in carbon disulphide soln.

Lead chromate was prepared by J. von Liebig, B. Legg, E. F. Anthon, M. Riot and B. Declisse, A. Scheurer, H. Hetherington and W. A. Allsebrook, and C. O. Weber by the action of soln. of the alkali chromates on lead sulphate. J. A. Atanasiu found that the electrometric titration of soln. of lead nitrate and potassium chromate gives a curve with a break corresponding with normal lead chromate. J. Milbauer and K. Kohn observed that the reaction: $PbSO_4+K_2CrO_4 \rightleftharpoons K_2SO_4+PbCrO_4$ progresses from left to right rapidly, and from right to left, slowly. The velocities of the reactions increase with temp. The equilibrium constant $K=[K_2CrO_4]/[K_2SO_4]$ is 0·000277 at 20°; 0·000365 at 40°; 0·000440 at 70°; and 0·000505 at 98·5°. No evidence of the formation of double salts was observed. The isothermal diagram has the form shown in Fig. 55, where *A* represents the solubility of potassium

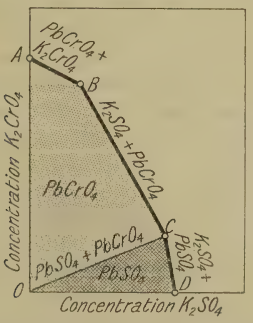


FIG. 55.—Isothermal Diagram for the System: $PbSO_4+K_2CrO_4 \rightleftharpoons K_2SO_4+PbCrO_4$.

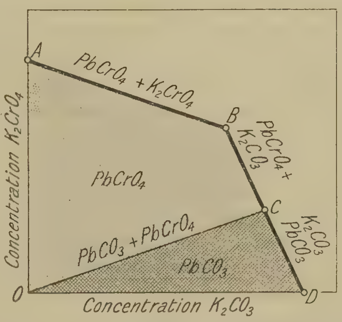


FIG. 56.—Isothermal Diagram for the System: $PbCO_3+K_2CrO_4 \rightleftharpoons K_2CO_3+PbCrO_4$.

chromate; and *D*, that of potassium sulphate. The regions of stability of the solid phases $PbCrO_4$, and $PbSO_4$ are shaded in the diagram. The curve *AB* represents a system in equilibrium with the four phases—$PbCrO_4$, K_2CrO_4, soln. and vapour; *BC*, a system in equilibrium with the four phases $PbCrO_4$, K_2SO_4, soln. and vapour; and *CD*, a system with the four phases $PbSO_4$, K_2SO_4, soln. and vapour in equilibrium. The four salts cannot exist side by side in the presence of their sat. soln. as the system would be invariant—**1**. 9, 5. At the point *C* there are six phases, $PbCrO_4$, K_2CrO_4, K_2SO_4, $PbSO_4$, soln. and vapour, in equilibrium. Adsorption is very marked at the low temp. and high concentration. It is inferred that the manufacture of chrome-yellow can be carried out from lead sulphate, and that various shades can be obtained by varying the conditions, temp., conc., and time. In the manufacture, an excess of lead acetate should be used, to secure the absence of adsorbed potassium chromate in the product, otherwise this chromate would rapidly convert the lead sulphate which is necessary for the particular shade, into lead chromate, and so the shade would be changed. J. G. Gentele's theory which explains the stability of chrome-yellow by the existence of a lead sulphatochromate is unlikely, since the present experiments make the existence of these double salts extremely doubtful.

F. Kuhlmann, C. O. Weber, and A. Winterfeld obtained lead chromate by the action of potassium chromate or dichromate on white-lead, or lead carbonate. H. Golblum and G. Stoffella studied the system: $PbCO_3+K_2CrO_4 \rightleftharpoons PbCrO_4+K_2CO_3$. The product nearly always contains a little lead carbonate. The isothermal diagram shown in Fig. 56, is analogous to that for the system indicated in the preceding diagram, Fig. 55. The mixture on the right of the equation $PbCO_3+K_2CrO_4 \rightleftharpoons PbCrO_4+K_2CO_3$, is more stable than that on the left. The equilibrium constant, $K=[K_2CO_3]/[K_2CrO_4]$, decreases with dilution on account of the disturbing effect of ionization. No compound or solid soln. of potassium chromate and lead chromate is formed, but the solubility of potassium carbonate decreases as the amount of lead carbonate in the solid residue and in soln. increases. A double compound of $K_2CO_3.PbCO_3$ appears to exist. The constant *K* at 25° is 5·46, and at 40°, 3·405. The thermal value of the reaction: $PbCO_3+K_2CrO_4=PbCrO_4+K_2CO_3$ is 5·822 Cals. If the equilibrium constant, *K*, Fig. 57, be represented by $K=Oa$, and the soln. of lead nitrate be added to a mixed soln. of potassium carbonate and chromate, when the ratio of $CO_3 \mid CrO_4$ is *greater* than *Oa*, lead carbonate alone will be precipitated until the ratio of the constituents remaining in soln. is equal to *Oa;* and conversely if the ratio be *less* than *Oa*, lead chromate alone will be precipitated. If the ratio be equal to *Oa*, and more than *Ob* of lead nitrate be added, a mixture of lead carbonate and chromate will be precipitated. On adding lead nitrate soln. to a mixed soln. of potassium chromate and carbonate, the precipitation of lead chromate or carbonate does not take place in such a way as to produce the predetermined ratio in the dissolved potassium salts. Whilst the interaction of lead carbonate and potassium chromate proceeds smoothly to an equilibrium, the interaction of lead chromate and potassium carbonate presents periodic phenomena. The curve representing the amount of potassium chromate formed oscillates with decreasing amplitude until the equilibrium is finally attained. This is attributed to the formation of a basic chromocarbonate of lead. On boiling lead chromate in potassium carbonate soln., a rhombic, ruby-red, crystalline solid is obtained with the composition: $3PbO.2CrO_3.2PbCO_3$. O. Ruff and E. Ascher studied the joint precipitation of lead and barium chromates; and lead sulphate and chromate; and O. Ruff, the X-radiograms.

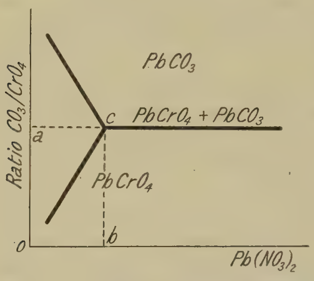


FIG. 57.—Mutual Precipitation of Lead Chromate and Carbonate.

N. S. Manross obtained crystals of lead chromate by melting lead chloride with potassium chromate, and leaching out the lead chloride, with boiling water. L. Bourgeois said that the yield is small because of the formation of the complex salt, $PbCl_2.PbCrO_4$. A better result is obtained by using potassium dichromate, but even then the result is not satisfactory. B. Redlich treated lead hydroxide with a soln. of sodium chromate or dichromate. The tint of the product is influenced by the presence of acetic acid, sodium sulphate, etc. F. Auerbech and H. Pick obtained lead chromate by treating basic lead chromate with a dil. aq. soln. of sodium hydrocarbonate and chromate; and M. Gröger, by the action of water on potassium lead chromate. D. G. Fitzgerald and R. C. Molloy roasted chromic oxide or chromite with lead oxide; and J. Milbauer said that there is a 100 per cent. conversion to chromate when a mixture of chromic oxide and lead oxide or carbonate is heated to 480° in oxygen at 12 atm. press. G. Chancel obtained lead chromate by warming a soln. of chromic oxide in alkali-lye with lead dioxide, and treating the filtrate with acetic acid. H. Vohl heated lead nitrate and chromic oxide in a crucible; and K. Toabe treated lead with a soln. of chromic and nitric acids at 60° to 140°. A. C. Becquerel obtained crystals of the salt by placing a Pb–Pt-couple in a soln. of chromic chloride in a sealed tube.

C. Lückow prepared lead chromate by an electrolytic process. The electrodes are formed of soft lead and the electrolyte is composed of a 0·3 to 3·0 per cent. soln. of sodium chlorate (perchlorate, nitrate, or acetate) 80 parts and sodium chromate 20 parts. The current density was 0·5 amp. per sq. dm. The colour of the deposit varies with the nature of the soln., being yellow in an acidic soln., and inclining to red in an alkaline soln.; electrodes about 10 to 20 mm. apart, and 1·5 to 1·6 volts are needed for weakly acid soln.; about 1·7 volts for neutral soln., and 2 volts for weakly alkaline soln. M. le Blanc and E. Bindschedler found that in the electrolysis of soln. of sodium chlorate and chromate, containing 1·5 to 12 per cent. of salt—of which 70 to 90 per cent. is chlorate—by means of a lead anode, lead chromate is formed near the anode, separating from it by its own weight, whereas in soln. containing a large proportion of chromate an adherent layer of chromate and lead dioxide forms on the anode. The yield of lead chromate is theoretical in the first case, practically zero in the latter. Sodium nitrate, acetate, or butyrate give practically the same result as chlorate. With the mixed electrolyte, the current is mainly transported by ClO'_3-ions, the chromate ions are therefore soon removed almost completely from the electrolyte in contact with the anode, and the precipitation of lead chromate takes place at some small distance from it. With a more conc. chromate soln., this is not the case. K. Elbs and R. Nübling found that in the electrolysis of very dil. soln. of chromic acid with lead electrodes, lead chromate alone is obtained; with more conc. soln.—up to 40 or 50 per cent.—there is evidence of the formation at the anode of **plumbic chromate,** $Pb(CrO_4)_2$, or of a mixture of lead chromate and dioxide; and with very conc. soln.—130 grms. of CrO_3 per 100 c.c.—a soln. is obtained which evolves oxygen when kept and deposits lead dichromate. The quantity of oxygen evolved is in agreement with $Pb(Cr_2O_7)_2 = PbCr_2O_7 + 2CrO_3 + O$. According to G. Just, the potential difference between a lead anode and a soln. containing bivalent lead ions depends very much on the anodic current density (probably owing to local increase of the conc. of the lead ions) so that at high current densities it may rise to the normal value for lead dioxide. When this is the case, lead dioxide is, of course, formed on the anode. B. Huick electrolyzed a 1·5 per cent. soln. of a mixture of sodium chlorate (95 parts) and sodium dichromate (5 parts) for lead chromate.

As pointed out by E. E. Free, by using very dil. soln. of lead nitrate and potassium chromate—say M- to $\frac{1}{256}M$-soln.—yellow **colloidal solutions** are obtained which are stable for some days; and, if glue be present, the soln. are stable for many months. J. Milbauer and K. Kohn also found that in the presence of acetic acid, or when boiled, the colloidal lead chromate is flocculated. F. W. O. de Coninck observed that when crystalline lead chromate is boiled for one-half to one hour with a very conc. soln. of pure potassium nitrate and immediately filtered, the filtrate exhibits a well-marked red fluorescence and contains lead chromate. If, however, the filtrate after some moments is refiltered, the filter retains the lead chromate, and the second filtrate is colourless. Sodium nitrate behaves similarly, but much more slowly. It is thus inferred that the lead chromate is rendered colloidal by the nitrate soln. but that the colloidal form re-polymerizes very rapidly. W. Lenze obtained colloidal soln. by mixing 25 grms. of a 10 per cent. soln. of sodium protalbinate (or lysalbinate) with 15 grms. of a 20 per cent. soln. of lead acetate, and treating a soln. of the precipitate in soda-lye with a conc. soln. of potassium chromate, and adding enough acetic acid to prevent precipitation. The soln. was dialyzed. It is greenish-yellow in reflected light, and brown, in transmitted light. J. N. Mukherjee and H. L. Ray studied the adsorption of salts by precipitated lead chromate.

A. Drevermann obtained crystalline lead chromate by the very gradual diffusion of very dil. soln. of potassium chromate and lead nitrate into water. The solids were placed in separate cylinders, placed in a wide dish, and the dish filled with water above the tops of the cylinders. If air is present, some basic salt may be precipitated. L. Bourgeois said that besides the crystalline chromate some amorphous basic chromate may be precipitated. H. Vohl also obtained the crystals by allowing soln. of a lead salt and a chromate to diffuse into each other through a porous diaphragm. E. Hatschek studied the **rhythmic precipitation** of lead chromate. A small quantity of 0·5 per cent. soln. of potassium dichromate is introduced into a tube containing a one per cent. agar-agar jelly containing 0·1 per cent. of lead acetate. The diffusion of the soln. into the jelly is accompanied by the formation of a stratified system. If a second small quantity of dichromate is added when the first has completely disappeared, it is found that the diffusion of the newly-added dichromate gives rise to a second system of strata, in which the successive bands are much broader than those in the first system. The fact that two different systems can be obtained in the same jelly is considered to be irreconcilable with the supersaturation theory which has been advanced to account for the formation of these stratified systems. The subject was investigated by R. E. Liesegang, E. R. Riegel and L. Widgoff, S. C. Bradford, E. Hatschek, P. B. Ganguly, V. Moravek, A. C. Chatterji and N. R. Dhar, D. N. Ghosh, and K. Ando.

The mineral crocoite occurs crystalline, and in imperfectly columnar or granular masses coloured various shades of bright hyacinth-red, or orange-red. The crystals are feebly pleochroic. The **colour** of the artificial crystals is also orange-red. When the crystals are finely powdered, the colour is yellow, like that of the precipitated cryptocrystalline or amorphous powder. Normal lead chromate, prepared by precipitation, is a clear yellow and its use as a pigment explains why so many investigations have been made on processes of manufacture with the object of increasing the purity and clarity of the colour of *chrome-yellow*—light, medium, and dark. Some of these terms are also applied to other chromate yellows, *jaune de chrome*, *giallo di cromo*, *amarillo de cromo*, or *Chromgelb*—light, medium, and dark. It also has the trade-names *Paris yellow*, *King's yellow*, a term also applied to orpiment. The paler tints—*lemon-chrome*, and *citron-chrome*—are produced by mixing lead chromate with lead sulphate. By increasing the basicity of the chromate the colour is deepened, and reddened ; so that an unbroken series of colours can be obtained varying from the pure yellow of the normal chromate to the deep orange-red of the basic salt—*orange-chrome*, *chrome-red*, which also has the trade-names *chrome-cinnabar*, *chrome-garnet*, *chrome-ruby*, *Austrian red*, *Vienna red*, *Derby red*, *American Vermilion*, *rouge de Perse*, etc. The variations of colour among different samples of the same compound may be greater than with different compounds. The variation in colour may be due to differences in the basicity, hydration, average grain-size, etc. ; and it is conditioned by the temp., and conc. of the soln., by the time occupied in the precipitation ; and by the nature of the soln. which in turn affects the salts adsorbed by the precipitated chromate. The subject was discussed by J. Milbauer and K. Kohn, L. Bock, C. O. Weber, K. Jablczynsky, J. W. Bain, F. Rose, G. Zerr, G. Zerr and G. Rübencamp, E. Guignet, J. G. Gentele, and J. Bersch. E. E. Free said that for clear yellow colours, the formation of basic salts must be avoided. The presence of a slight trace of alkali, or a higher temp. than usual, may cause a darkening of the yellow colour. This darkening is produced by a number of unrecognized causes, but P. Grouvelle, and M. Dullo considered that in many cases the alteration of the colour is a visible sign that the normal chromate has undergone a partial change to the basic condition, produced by the presence of alkali. This is confirmed by the fact—observed by S. M. Godon de St. Menin, L. N. Vauquelin, C. O. Weber, and H. W. Hofmann—that the presence of small amounts of free acid in the soln. lessens the tendency for the colour to turn. C. O. Weber also noticed that an excess of chromate in the precipitating soln. favours the tendency of the colour to change, while an excess of lead salt acts in the converse way; but M. Dullo does not agree with this statement. E. E. Free suggested that in some cases the darkening of the colour may be due to the growth of the fine granules into coarser grains. The darkening of the colour may render the chrome-yellow quite useless for a pigment.

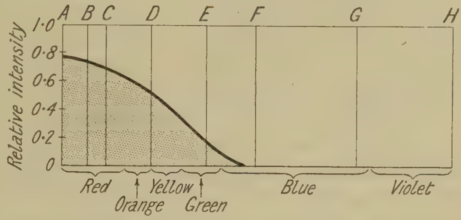


Fig. 58.—The Spectrum of Light Reflected from Lead Chromate.

E. E. Free showed that the difference in the colour of the yellow colour of the powder and the orange colour of the crystals is due to differences in the grain-size. The largest crystals are obtained with hot dil. soln. The size of the precipitated crystals increases continuously with decrease in conc. The colours of the precipitates obtained from the most conc. and the most dil. soln. are lighter than is the case with precipitates from soln. of intermediate conc. The curve shows a maximum depth of colour at moderate conc. So that size of grain alone does not suffer to explain the results. It is assumed that the basicity as well as grain-size were concerned in the effects obtained. A. Habich, T. Gobel, and J. Bersch showed that the larger crystals of the basic chromates correspond with the deeper and redder shades of colour; and W. E. Fuss stated that chrome-red, when ground, acquires a yellow tinge. B. Redlich said that chromates prepared by the action of chromate soln. on lead hydroxide are redder when the hydroxide is crystalline. E. L. Nichols and B. W. Snow showed that the reflection spectrum of pigments is produced by light reflected from the surface, and by light reflected from the interior faces. That reflected from the surface is white; and that reflected from the interior determines the colour of the pigment. The internally reflected light is that light which has entered at least one of the crystals and been reflected from the posterior surface of that crystal or from the surface of some other crystal situated more deeply within the mass. E. E. Free continued: with a more finely powdered pigment, there will be obviously more surface per unit of mass, and the first of these interior faces will be on the average nearer the external surface of the layer, that is, the layer of coloured material through which the internally reflected ray must pass, is less in the finely powdered material. It must therefore happen that the selective absorption which takes place in this ray will be relatively weaker, or in common phrase the "colour" imparted to the ray will be less marked. Crystalline lead chromate, however, changes from a reddish-orange to a clear yellow when powdered; so that there appears to be not only a weakening of the colour, but an actual change from red or orange into yellow. E. L. Nichols found that when light is reflected from a thin plate of lead chromate, the blue and violet, most of the green, and a considerable fraction of the yellow are absorbed, but the red is allowed to pass in greater degree and in increasing proportion with increasing wave-length. This is shown by Fig. 58, where the abscissæ represent wave-lengths, and the ordinates of the intensities of the reflected light in terms of uniform white light. The green component of the light which reaches the eye is masked by the larger proportion of red, and the apparent colour is a shade of yellow or orange tinged with red. By increasing the thickness of the plate, the area representing the absorbed light extends towards the left, thus concentrating the red and reducing the yellow. Conversely when the thickness of the plate is decreased, the green progressively weakens the red and makes the yellow more prominent in the transmitted light. As the transmitted light extends into the blue, a further decrease in the thickness of the plate, the blue tends to neutralize the yellow, as the green neutralizes the red, and the yellow becomes paler and paler, until in the limiting case the colour appears white. L. Godard studied the effect of radiant heat rays by chrome-yellow. Lead chromate belongs to the class of substances which W. Ackroyd called metachromatic because they change their colour on heating. The colour was shown by R. F. Marchand, L. Bourgeois, and E. J. Houston and E. Thomson to change from yellow to orange to red, and in this respect, it behaves like the majority of other substances observed by C. F. Schönbein, and E. J. Houston and E. Thomson, in that the maximum intensity, with rise of temp., moves towards the red. The basic chromates also become a deeper red when heated. Conversely, as the yellow chromate is cooled to —30° to —40°, it becomes yellowish-green; and M. Bamberger and R. Grengg said that both the natural and artificial crystals are decolorized at —190°.

The **crystals** of crocoite are monoclinic prisms; and, according to H. Dauber, the axial ratios are $a:b:c=0{\cdot}9603:1:0{\cdot}9159$, and $\beta=102°\ 27'$; E. F. Chirva gave $a:b:c=0{\cdot}960293:1:0{\cdot}91305$, and $\beta=77°\ 32'\ 55''$. The crystals are usually prismatic, but the habit varies so that the crystals sometimes resemble acute rhombohedra. The faces are usually smooth and brilliant; the (110) face may be vertically striated. The (110)-**cleavage** is distinct; but the (001)- and (100)-cleavages are not so well defined. The crystals were also examined by N. von Kokscharoff, and F. Hessenberg. A. de Schulten, A. Drevermann, and L. Bourgeois also showed that the artificial crystals are monoclinic prisms. B. Gossner and F. Mussgnug showed that the **X-radiograms** correspond with $a=6{\cdot}82$ A., $b=7{\cdot}48$ A., $c=7{\cdot}16$ A., and $\beta=102°\ 33'$; or $a:b:c=0{\cdot}912:1:0{\cdot}957$. The vol. of unit cell is $356{\cdot}5\times10^{-24}$ c.c. G. Tammann and Q. A. Mansuri found that the recrystallization of the powder with granules less than 0·3 mm. begins between 237° and 248°. The **optical character** is positive; and the **optic axial angle** $2V=54°$. In accord with the dimorphism of lead sulphate, discussed by W. Grahmann, P. Groth and K. Haushofer said that lead chromate is probably dimorphous furnishing monoclinic and rhombic crystals. C. Lüdeking obtained artificially what he regarded as rhombic crystals—*vide supra*. According to F. M. Jäger and H. C. Germs, lead chromate is trimorphic. The monoclinic or α-form is stable below 707°; the β-form is stable between 707° and 783°; and the γ-form between 783° and the m.p. 920°—Fig. 62. The transition $\alpha\text{-PbCrO}_4\rightleftharpoons\beta\text{-PbCrO}_4$, at 707°, is attended by a small thermal change, while the transition $\beta\text{-PbCrO}_4\rightleftharpoons\gamma\text{-PbCrO}_4$, at 783°, involves a greater thermal change. Some varieties of crocoite showed only one transition temp. at 792°.

C. H. D. Bödeker gave 5·951–6·004 for the **specific gravity** of lead chromate; L. Playfair and J. P. Joule, 5·653; and P. Niggli, 6·123. H. G. F. Schröder gave 5·965 for the sp. gr. of crocoite; and for the artificial crystals, N. S. Manross gave 6·118; A. de Schulten, 6·123 at 15°; L. Bourgeois, 6·29; J. Milbauer and K. Kohn gave 5·44 for that of the amorphous precipitate. B. Gossner and F. Mussgnug calculated 6·00 for the sp. gr. The **hardness** of crocoite is 2·5 to 3·0. P. W. Bridgman found the linear **compressibility** at 30°, in the direction C of the monoclinic crystals, to be $\delta l/l_0=0{\cdot}0_64978p-0{\cdot}0_{11}378p^2$, and at 75°, $\delta l/l_0=0{\cdot}0_65102p-0{\cdot}0_{11}422p^2$ for press. p ranging up to 12,000 kgrms. per sq. cm. H. Kopp gave 0·0900 for the **specific heat** between 19° and 50°; and 29·0 for the mol. ht. T. M. Lowry and L. P. McHatton observed that the fineness of the powder produced by the decrepitation of crocoite depends on the proportion of included water which the mineral contains. R. F. Marchand said that lead chromate fuses at a red-heat and, on cooling, solidifies to a dark brown mass which forms a brownish-yellow powder ; but if the molten chromate be poured into cold water, it forms a red mass which yields a red powder. F. M. Jäger and H. C. Germs found that the **melting point** of lead chromate is 844°—and fusion is attended by a little decomposition ; while crocoite melts at 835° to 839°. R. F. Marchand said that when heated above its m.p., it gives off about 4 per cent. of oxygen forming lead dichromate and chromic oxide. The amount of oxygen evolved is only a fractional part of that which would be evolved if the decomposition were complete. R. F. Marchand represented the reaction : $4PbCrO_4=2Pb_2O(CrO_4)+Cr_2O_3+3O$; C. Schubert, and W. Hempel and C. Schubert found that the evolution of gas begins at about 600°, and he observed rather more oxygen is given off up to 1150° than is required by this equation. If re-heated in oxygen gas, the chromate is not reformed ; but if a mixture of chromic oxide and lead oxide be heated in oxygen, 14·9 parts of oxygen are taken up for 100 parts of chromic oxide. W. Hempel and C. Schubert found that dissociation begins at about 600°, and is completed at 1150°. R. Lorenz and W. Herz studied some relations between the b.p. and the critical temp. H. C. Sorby gave 2·730 for the **index of refraction** of crocoite ; C. Bärwald gave 2·203 and 2·667 for red-light, and 2·437 and 2·933 for green-light ; while A. des Cloizeaux gave 2·42 for yellow-light. A. de Gramont examined the **spark spectrum** of crocoite. G. H. Hurst found that chrome-yellow reflects a large proportion of the yellow and green rays, with a small quantity of orange and blue rays, Fig. 59. G. I. Pokrowsky studied the polarization of light by finely divided lead chromate suspended in water. W. W. Coblentz gave for the diffuse reflecting power :

λ . . .	0·54μ	0·60μ	4·4μ	8·8μ	24·0μ
Emission .	61·2	70·2	41·2	4·74	7·4

T. W. Case said that the **electrical resistance** of crocoite exceeds one megohm, and is not affected by light. The sp. **electrical conductivity** of a sat. soln. at 18° was found by F. Kohlrausch to be of the order $0·1\times10^{-6}$ mhos. According to J. Rosenthal, the electrical conductivity of the compressed powder increases with temp., being 0·110 mho at 208°, and 0·385 mho at 331°. The precipitated powder is a better conductor than that obtained by grinding the fused chromate. R. Labes studied the electrical charges on the surface of lead chromate in soln. of electrolytes.

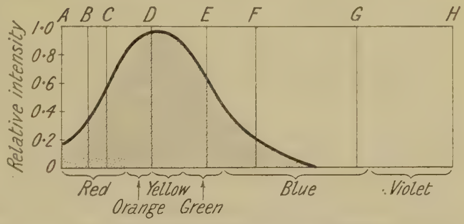


Fig. 59.—Reflection Spectrum of Chrome-yellow.

E. Rutherford and F. Soddy observed that red-hot lead chromate has no action on **radium or thorium emanation.** R. F. Marchand observed that when lead chromate is heated in **hydrogen,** water is formed and the mass becomes incandescent before the temp. of the vessel had attained a red-heat. The reaction is symbolized $2PbCrO_4+5H_2=5H_2O+Cr_2O_3+2Pb$. H. Mennicke found that hydrogen *in statu nascendi*—from hydrochloric acid and zinc in the presence of platinum—reduces lead chromate quickly and completely. J. Milbauer and K. Kohn said that when the yellow chromate is warmed with **water** it becomes red, but on cooling the yellow colour is restored ; and A. J. Cox found that at 25°, the chromate is hydrolyzed so that the water contains about 0·02 millimol of chromic acid per litre. J. F. G. Hicks and W. A. Craig studied the progressive hydrolysis of lead chromate by water at 100° at ordinary press., and in sealed tubes ; and found that the reaction is complete in about 3 hrs. A basic lead chromate is formed. The older chemists thought that lead chromate is insoluble in water, but A. Drevermann found that 1000 parts of water dissolve 0·02 part of salt; and P. Harting said that lead nitrate is precipitated as chromate when one part is present in 70,000 parts of water. G. von Hevesy and F. Paneth gave for the solubility $1{\cdot}2\times10^{-5}$ grm. per litre at 25°; G. von Hevesy and E. Rona gave 2×10^{-7} mol per litre at 20°; F. Kohlrausch and F. Rose, 0·0002 grm. per litre at 18°; F. Kohlrausch, 0·0001 grm. per litre at 18°; K. Beck and P. Stegmüller, 3×10^{-7} mol per litre at 25°. F. Auerbach and H. Pick gave for the solubility product, $[Pb''][CrO_4'']=2\times10^{-14}$ at 18°; and $[Pb'']^2[CrO_4''][OH']^2=6\times10^{-35}$. P. Schützenberger observed that when heated in a porous crucible over a gas-flame, lead chromate adsorbs moisture which is expelled only at a red heat. K. B. Lehmann observed that conductivity water dissolves more than distilled water. According to L. N. Vauquelin, lead chromate dissolves completely in a soln. of **potassium hydroxide**; and F. Wöhler and J. von Liebig added that the soln., sat. while hot, deposits after a few days yellowish-red laminæ of a basic salt. A. Drevermann also said that a soln. of potassium hydroxide makes the crystals opaque, and darker, and they are then slowly dissolved. M. Lachaud and C. Lepierre found that a litre of $2N$-KOH dissolves 11·9 grms. of lead chromate at 16°; 16·2 grms. at 60°; 26·1 grms. at 80°; and 38·5 grms. at 102°, forming $K_2Pb(CrO_4)_2$. Conc. potash-lye—say 45 per cent. KOH, sp. gr. 1·47—forms oxychromate, or lead monoxide; but $2N$-KOH forms only the oxychromate. Molten potassium hydroxide forms crystals of the oxychromate—*vide infra*, basic salts. R. Eberhard observed that the salt is soluble in an alcoholic soln. of potassium hydroxide. According to F. Brandenburg, when lead chromate is boiled with a soln. of **potassium carbonate**, a basic oxychromate is formed, and then lead carbonate; the liquid takes up much chromic and lead oxides, and when treated with sulphuric acid, lead chromate is precipitated. The observations of H. Golblum and G. Stoffella on the equilibrium $PbCrO_4+Na_2CO_3\rightleftharpoons PbCO_3+Na_2CrO_4$ have been summarized in Fig. 60. K. B. Lehmann found that a dil. soln. of sodium carbonate readily dissolves lead chromate and a state of equilibrium is inaugurated with the oxychromate: $2PbCrO_4+2Na_2CO_3+H_2O\rightleftharpoons PbO.PbCrO_4+2NaHCO_3+Na_2CrO_4$. With increasing dilution and rise in temp. the equilibrium is displaced towards the right-hand side of the above equation. When the equilibrium is approached from the side of the basic lead chromate, exactly the same results are not obtained as from the side of the normal lead chromate. The reversible reaction expressed by the equation: $PbCrO_4+Na_2CO_3\rightleftharpoons PbCrO_3+Na_2CrO_4$, only takes place in the presence of considerable quantities of hydrocarbonate in soln., otherwise basic lead chromate is formed. For soln. with the total sodium conc. from $0{\cdot}05N$- to $0{\cdot}1N$-Na_2CO_3, at 18°, the equilibrium constant, for the reaction $2PbCrO_4+2CO_3''+H_2O\rightleftharpoons PbO.PbCrO_4+CrO_4+2HCO_3'$ is $[CrO_4''][HCO_3']^2/[CO_3'']^2=0{\cdot}057$—$CQ'$, Fig. 60; for $2PbCO_3+CrO_4''+H_2O\rightleftharpoons 2HCO_3'+PbO.PbCrO_4$, it is $[HCO_3']^2/[CrO_4'']=1{\cdot}95$—$Q'B$, Fig. 60; and for $PbCrO_4+CO_3''\rightleftharpoons CrO_4''+PbCO_3$, it is $[CrO_4'']/[CO_3'']=0{\cdot}2$—$AQ'$, Fig. 60; and if carbonic acid be present, $[H_2CO_3][CrO_4'']/[HCO_3]^2=4\times10^{-5}$. Lead chromate enters into reversible reaction with a soln. of sodium hydrocarbonate according to the equation: $PbCrO_4+2NaHCO_3\rightarrow PbCO_3+Na_2CrO_4+CO_2+H_2O$; equilibrium is attained at a much lower press. of carbon dioxide than is the case with lead sulphate. The equilibrium conditions for the ternary system: Na_2CO_3–$NaHCO_3$–

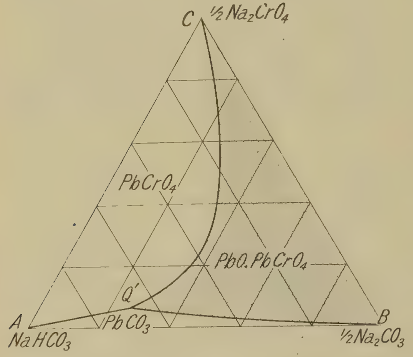


Fig. 60.—Equilibrium between Lead Chromate and $0{\cdot}1N$-Sodium Carbonate Solutions at 18°.

Na_2CrO_4 in the presence of lead chromate, oxychromate and carbonate, are shown in Fig. 60. The region where lead carbonate is stable is very small, and the transformation $PbCrO_4+Na_2CO_3\rightleftharpoons PbCO_3+Na_2CrO_4$ occurs only in the presence of hydrocarbonate. The regions of stability of the two lead chromates are very wide.

H. Moissan observed that **hydrogen chloride** decomposes lead chromate forming red fumes of chromyl chloride ; and H. Schwarz, that hot **hydrochloric acid** dissolves the chromate with the formation of chlorine, lead chloride, and chromic chloride. M. Gröger said that hot, dil. hydrochloric acid decomposes the chromate completely forming lead chloride which, if not filtered off, and water be added, re-forms lead chromate. K. Beck and P. Stegmüller found the solubility, S millimols per litre, to be :

	HCl	0·1*N*-	0·2*N*-	0·3*N*-	0·4*N*-	0·5*N*-	0·6*N*-
S	18°	0·186	0·393	0·654	1·07	1·56	2·25
	25°	0·239	0·485	0·839	1·32	4·06	2·95
	37°	0·337	0·744	1·31	2·10	3·28	4·69

so that, as indicated by K. B. Lehmann, the solvent action is greater, the more conc. the acid. A conc. soln. of sodium chloride dissolves traces of the chromate ; and M. Lachaud and C. Lepierre stated that molten sodium chloride converts the chromate into basic chromates. J. F. G. Hicks, and J. F. G. Hicks and W. A. Craig found that reactions in fused salts can be brought about to yield products analogous to those obtained with the same initial substances in aq. soln., the chief difference being the slowness of the reactions in the fused medium at 870°. The reaction with fused **sodium chloride** represents a true state of equilibrium. A basic chromate is the main product of the reaction. J. Milbauer and K. Kohn found that lead chromate reacts quantitatively with **potassium iodide :** $CrO_4''+8H^{\cdot}+3I'=Cr^{\cdots}+4H_2O+3I$. M. le Blanc and E. Bindschedler found lead chromate to be insoluble in contact with a 1·5 per cent. soln. of **sodium chlorate** for 4 hrs. at room temp. H. H. Willard and J. Kassner found that the solubility of lead chromate in **perchloric acid,** S grm. per 100 c.c. at 25°, is :

M-$HClO_4$	0·1	0·5	1·0	2·0	3·0	4·0	5·0
S	0·0041	0·0120	0·0140	0·0199	0·0211	0·0213	0·0191

The solubility is reduced if lead perchlorate or sodium dichromate be present.

J. B. Senderens said that the chromate is not altered when boiled for a week with water and **sulphur.** The presence of free sulphur, or **sulphides,** gradually darkens chrome-yellow owing to the formation of lead sulphide. E. F. Anthon heated in a glass tube a mixture of lead chromate with one-eighth of its weight of sulphur, and found that the product takes fire with incandescence on exposure to air, forming sulphur dioxide, and chromic and lead oxides. H. Moissan and P. Lebeau said that **sulphur hexafluoride** is not decomposed by molten lead chromate. Hot sulphuric acid decomposes lead chromate, forming lead sulphate, and H. Schwarz found that for complete decomposition an excess of 4 to 5 mols of sulphuric acid is necessary ; M. Gröger found that the decomposition with boiling dil. sulphuric acid is incomplete ; the cold conc. acid acts slowly while the hot acid acts quickly, forming chromic acid. J. Milbauer and K. Kohn's observations on the reaction with **potassium sulphate** soln. are summarized in Fig. 55. G. Chancel said that lead chromate is insoluble in a soln. of **sodium thiosulphate.**

E. C. Franklin and C. A. Kraus found that lead chromate is insoluble in liquid **ammonia ;** and W. E. Garrigues that it is insoluble in aq. ammonia. C. L. Parsons found that lead chromate favours the oxidation of ammonia by air. R. H. Brett said that the salt is insoluble in a soln. of ammonium chloride. A. Drevermann, J. von Liebig, and A. Baumann observed that lead chromate is insoluble in nitric acid. E. Duvillier stated that boiling conc. **nitric acid** dissolves 98·79 per cent. CrO_3 and only 1·21 per cent. PbO, while the remaining lead separates as lead nitrate. When water is added to the mixture, lead chromate is reformed. K. Beck and P. Stegmüller gave for the solubility S millimols Pb per litre, at 18°,

HNO_3	0·1N-	0·2N-	0·3N-	0·4N-	0·5N-	0·6N-
S	0·129	0·227	0·312	0·401	0·488	0·598

H. H. Willard and J. L. Kassner found the solubility of lead chromate, S grm. per 100 c.c. at 25°, in nitric acid, to be :

M-HNO_3	0·1	0·5	1·0	2·0	3·0	4·0	5·0
S	0·0063	0·0177	0·0385	0·0889	0·1701	0·2812	0·4367

The solubility is reduced if lead nitrate, or sodium dichromate be present. C. Marie said that 0·5 grm. of lead chromate dissolves in a mixture of nitric acid with 2 grms. of **ammonium nitrate.** F. Wöhler and J. von Liebig found that molten **potassium nitrate** converts lead chromate into the oxychromate ; and M. Lachaud and C. Lepierre observed the formation of the complex salts $K_2Pb(CrO_4)_2$ and $2PbO.K_2Pb(CrO_4)_2$. Similarly also with sodium and lithium nitrates. J. F. G. Hicks, and J. F. G. Hicks and W. A. Craig studied the reaction with an equimolar mixture of fused sodium and potassium nitrates at various temp. up to 230°. The reaction at different temp. represents states of equilibrium analogous to hydrolysis. The product of the reaction is a basic chromate. F. W. O. de Coninck studied the peptizing action of a boiling soln. of potassium nitrate on lead chromate—*vide supra.* K. Jellinek and H. Ens found that 3 drops of a one per cent. soln. of **silver nitrate** are coloured reddish-brown owing to the formation of silver chromate.

H. Moser observed that when heated with **carbon,** lead chromate is reduced to lead and chromic oxide. E. Berger and L. Delmas found that the combustion of carbon in air is facilitated by the presence of lead chromate. M. Tarugi found that at 400°, **calcium carbide** reduces the chromate to a calcium lead alloy and chromium. A. Kutzelnigg observed that lead chromate exerted an oxidizing action on a soln. of **potassium ferrocyanide ;** and J. R. Campbell and T. Gray, that the salt exerts an oxidizing action on **methane** and **ethylene.** K. B. Lehmann found that conc. **acetic acid** dissolves very little lead chromate ; and A. Baumann, that acetic acid dissolves no chromate. Lead chromate is almost insoluble in a soln. of **ammonium acetate ;** and, according to I. M. Kolthoff, in a soln. of **sodium acetate.** H. C. Bolton found that a boiling conc. soln. of **citric acid** decomposes crocoite. J. Spiller said that lead chromate is not precipitated in the presence of **alkali citrates ;** and A. Naumann, that it is insoluble in acetone. J. B. Charcot and P. Yvon said that **saliva** dissolves perceptible amounts of lead chromate. L. Vignon stated that fabrics are usually dyed with lead chromate by passing the material through the aq. soln. of a soluble lead salt and then through a soln. of potassium or sodium chromate. Dyeing also occurs if the material is agitated in a suspension of precipitated lead chromate in water ; equally good results are obtained with silk, wool, or cotton. The lead chromate does not combine chemically with the material dyed. Dyeing also takes place if the lead chromate is suspended in alcohol or benzene, but the resulting colours are not so deep as those obtained when water is the medium of suspension. The reaction was studied by M. A. Iljinsky and V. V. Kozloff.

P. Jannasch observed that natural **silicates** are decomposed when heated strongly with lead chromate. L. Kahlenberg and W. J. Trautmann found that when mixed with silicon and heated by a bunsen burner a sudden reaction occurs with the evolution of heat and light. There is a strong reaction at a " cherry " red-heat and when heated in the electric arc. E. Lay found that **silicon hydrotrinitride** reduces lead chromate at a high temp. M. Lachaud and C. Lepierre found that a soln. of **chromic acid** causes amorphous lead chromate to crystallize, or, according to K. Preis and B. Rayman, to be transformed into lead dichromate ; but, according to W. Autenrieth, a hot, conc. soln. of chromic acid does not dissolve the chromate.

J. Coneybeare said that lead chromate dissolves sparingly in water containing **potassium chromate.** F. Paneth and co-workers, G. M. Schwab and E. Pietsch, and A. Eisner studied the adsorption of radioactive substances by crystals of lead chromate. J. N. Mukherjee and H. L. Ray found that a precipitate of lead chromate in contact with various salts becomes negatively charged in contact with water, this being due, probably, to the adsorption of chromate ions or, alternatively, to the adsorption of hydroxyl ions from the water. The velocity of electrical-osmosis shows that when the lead chromate is in contact with soln. of potassium chromate, iodate, nitrate, iodide, sulphate, and chloride, lead nitrate, barium chloride, and calcium chloride of conc. varying between 0·000067*N* and 0·004*N*, the order of adsorbability of the cations is $Pb^{\cdot\cdot} > Ba^{\cdot\cdot} > Ca^{\cdot\cdot} > K^{\cdot}$, whilst with a constant cation, $K^{\cdot}$, the order of adsorption of the anions is that given above. The constituent ions of a precipitate are very strongly adsorbed by it, those of lead being so largely adsorbed as to reverse the charge at a conc. of 0·00005*N*. These observations cannot be explained on the type of adsorption assumed by F. Paneth; and the suggestion of K. Fajans and K. von Beckerath that there is a parallelism between the intensity of adsorption of the anion and the solubility of the salt of the adsorbed ion with opposite sign in the precipitate is not tenable, since the nitrate is more strongly adsorbed than the iodide or sulphate, whereas the order of increasing solubility of the lead salts is $CrO_4'' < IO_3' < I' < SO_4'' < Cl' < NO_3'$. F. M. Jäger and H. C. Germs studied the binary system: **lead sulphate**—and lead chromate, and obtained the diagram, Fig. 61, which is largely conjectural because of the decomposition at the higher temp. There is a gap in the solid soln. between 30 and 40 per cent. $PbCrO_4$. The mixed crystals have transition points at 934°, 874°, and 748°.

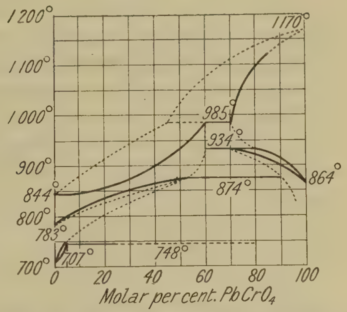


FIG. 61.—Freezing-point Curves of the Binary System: $PbSO_4$–$PbCrO_4$.

A number of **basic lead chromates** has been reported. C. Lückow, and J. J. W. Watson and T. Slater obtained basic salts by the electrolysis of a soln. of sodium chlorate and chromate with lead electrodes; S. Ganelin, by the action of potassium chromate and magnesia on lead sulphate; A. C. Becquerel, by the action of a zinc plate and water on lead chromate; E. Toelle and M. von Hofe, and J. Kronen, by the action of a paste of lead chromate on lead oxide; H. N. Holmes,

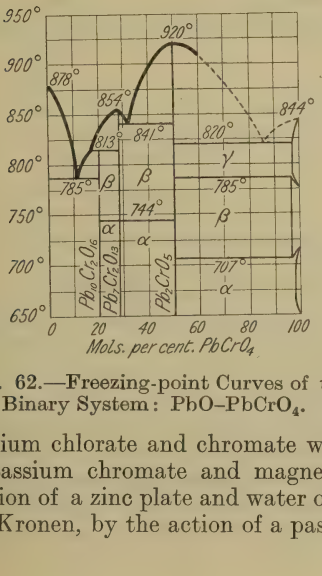


FIG. 62.—Freezing-point Curves of the Binary System: PbO–$PbCrO_4$.

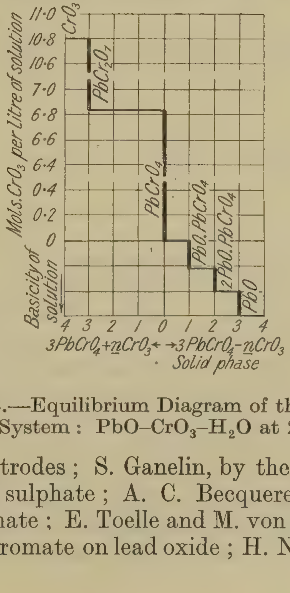
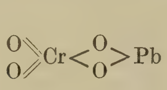


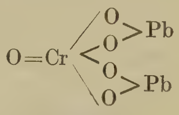
FIG. 63.—Equilibrium Diagram of the Ternary System: PbO–CrO_3–H_2O at 25°.

by the action of potassium chromate on soln. of lead salts; and A. Prinvault observed transient violet compounds of apparently high basicity. The equilibrium conditions of fused mixtures of lead oxide and chromate were studied by H. C. Germs, F. M. Jäger and H. C. Germs, J. F. G. Hicks. The f.p. curve of the binary system by F. M. Jäger and H. C. Germs is shown in Fig. 62. The compound Pb_5CrO_8, or $Pb_{10}Cr_2O_{16}$, has no real m.p. and is stable only below 815°. The eutectic between $PbCrO_4$ and Pb_2CrO_5 occurs at 820°, but this part of the diagram could not be accurately explored because of decomposition. The other basic salt was $Pb_7Cr_2O_{13}$. J. F. G. Hicks obtained Pb_2CrO_5, as well as Pb_4CrO_7; Pb_3CrO_6; and $Pb_3Cr_2O_9$ on his f.p. curve; but the results were obtained by a cruder method. The compounds obtained by the f.p. process, are not necessarily the same as those obtained by wet processes. The results of A. J. Cox's examination of the ternary system: $PbO–CrO_3–H_2O$ at 25°, are summarized in Fig. 63. Here, the basic salts Pb_3CrO_6 and $PbCrO_5$ were obtained—*vide supra,* mercury chromates.

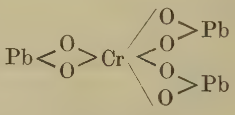
F. M. Jäger and H. C. Germs observed that **lead tetroxychromate,** $5PbO.CrO_3$; $4PbO.PbCrO_4$; Pb_5CrO_8; or $Pb_{10}Cr_2O_{16}$, is formed from mixtures of lead chromate with 82·5 to 89 molar per cent. of lead oxide, Fig. 62. The compound is stable below 815°. It decomposes with the evolution of oxygen above its m.p.; and at a temp. exceeding 615°, it decomposes into a liquid and solid β-$Pb_7Cr_2O_{13}$. J. F. G. Hicks obtained **lead trioxychromate,** $4PbO.CrO_3$; $3PbO.PbCrO_4$; or Pb_4CrO_7, from a molten mixture of lead oxide and chromate, but F. M. Jäger and H. C. Germs did not find it—Fig. 62. D. Strömholm added the calculated amount of $0·1N$-K_2CrO_4 to lead hydroxide, and as soon as equilibrium was established; there remained an ochre-yellow mass of small needles of the *monohydrate* of lead trioxychromates, $Pb_4CrO_7.H_2O$. F. M. Jäger and H. C. Germs observed the formation of **lead pentoxybischromate,** $7PbO.2CrO_3$; $5PbO.2PbCrO_4$; or $Pb_7Cr_2O_{13}$, by melting lead chromate with 68 to 82·5 molar per cent. of lead oxide, Fig. 62. It melts at 854° with feeble dissociation. At 774°, there is a reversible transformation with a small thermal change. It forms with lead oxychromate a eutectic at 841° and 68 molar per cent. PbO. They consider that the mineral *melanochroite* from Beresowsk, Urals, is probably this compound—*vide infra.* At 830°, this melanochroite decomposes with the separation of lead. J. F. G. Hicks reported **lead dioxychromate,** $3PbO.CrO_3$; $2PbO.PbCrO_4$; or Pb_3CrO_6, to be formed from fused mixtures of lead oxide and chromate, but F. M. Jäger and H. C. Germs did not find it. On the other hand, A. J. Cox observed its formation under the conditions indicated in Fig. 63. This salt can be regarded as a derivative of the hypothetical *orthochromic acid,* H_6CrO_6; just as $PbO.PbCrO_4$ can be regarded as a derivative of *parachromic acid,* H_4CrO_5.



$PbCrO_4$



$PbO.PbCrO_4$



$2PbO.PbCrO_4$

J. F. G. Hicks, however, does not favour this hypothesis, since it does not explain the constitution of $3PbO.PbCrO_4$.

P. L. Dulong prepared **lead oxychromate,** $2PbO.CrO_3$; $PbO.PbCrO_4$; or Pb_2CrO_5, by boiling lead oxide or carbonate with an aq. soln. of potassium chromate. M. Rosenfeld, F. Auerbach and H. Pick, T. Göbel, and J. G. Gentele employed modifications of this process—*cf.* Figs. 62, and 63. L. N. Vauquelin, and M. Faraday exposed to the air a dil. soln. of lead nitrate and potassium chromate in dil. potashlye, and obtained small crystals which was thought were the normal chromate, but which were shown by F. Wöhler and J. von Liebig to be the oxychromate. C. Reichard obtained the oxychromate by the action of potassium chromate on a soln. of lead sulphate in an aq. soln. of ammonium tartrate; R. Weinland and F. Paul, by the action of potassium chromate on a hot soln. of potassium hydroxychlorate; and A. A. Hayes, by the slow action of carbon dioxide on a soln. of lead oxide and potassium chromate in potash-lye. As the soln. becomes sat. with carbon dioxide, orange-yellow needles of lead oxychromate are formed. F. M. Jäger and H. C. Germs observed that this compound is formed by the fusion of mixtures of lead chromate with 15 to 68 molar per cent. PbO—Fig. 62. J. F. G. Hicks obtained it in a similar manner; and R. F. Marchand, by heating the neutral chromate to redness for some time. A. A. Hayes, J. F. G. Hicks, W. E. Fuss, J. F. G. Hicks and W. A. Craig, F. Wöhler and J. von Liebig, M. Gröger, L. Bourgeois, and M. Lachaud and C. Lepierre obtained it by fusing lead chromate with an alkali nitrate, and leaching out the soluble salt with water. M. Lachaud and C. Lepierre, and J. F. G. Hicks and W. A. Craig, by fusing a mixture of lead oxide and chromate, and sodium chloride. Lead oxychromate is also a product of the hydrolysis of the normal chromate with water or, according to E. F. Anthon, P. Grouvelle, J. F. G. Hicks, C. O. Weber, A. Habich, M. Lachaud and C. Lepierre, with dil. alkali-lye; or, according to F. Auerbach and H. Pick, with $0\cdot1N\text{-}Na_2CO_3$. P. L. Dulong, and E. Guignet obtained the same basic salt by boiling lead chromate and carbonate with water; M. Rosenfeld, T. Göbel, P. Grouvelle, and J. Badams, by boiling lead chromate and oxide with water; and J. J. Berzelius, by boiling lead oxide with potassium chromate and water. R. Weinland and R. Stroh prepared the basic chromate **lead dihydroxychromate,** $[Pb(OH)_2]CrO_4$, by double decomposition with lead perchlorate and a soluble chromate. The equilibrium conditions were studied by A. J. Cox—Fig. 63. Analyses were reported by D. Strömholm, M. Gröger, J. F. G. Hicks, M. Lachaud and C. Lepierre, F. Auerbach and H. Pick, J. Badams, etc. The colour of this basic chromate varies from a deep fiery red, cochineal-red, scarlet-red, orange-red, vermilion, etc. Orange-chrome —*vide supra*—is mainly this compound. It may be formed as an amorphous, or eruptic crystalline powder; and the crystals were described by M. Lachaud and C. Lepierre as prismatic needles, which, according to L. Bourgeois, are isomorphous with lanarkite. F. M. Jäger and H. C. Germs said that it furnishes no polymorphic transformation, and that it melts at 920°. The eutectic with lead chromate is at 820° with about 15 molar per cent. of lead oxide. M. Lachaud and C. Lepierre said that it is insoluble in water; and F. Auerbach and H. Pick gave 6×10^{-35} for the solubility product at 18°. M. Lachaud and C. Lepierre found that a litre of $2N$-KOH at 15° dissolves 10·1 grms.; at 60°, 13·5 grms.; at 80°, 21·9 grms.; and at 102°, 32·1 grms. Dil. acids transform it into lead chromate. Observations on the action of sodium hydrocarbonate soln., by F. Auerbach and H. Pick, are summarized in Fig. 56. J. Badams said that acetic acid extracts half the contained lead oxide.

R. Hermann reported the occurrence of a basic lead chromate in the limestone of Beresowsk, Urals, and he called it **melanochroite**—from μέλας, black; and χρόα, colour—but since the colour of the mineral is red, not black, E. F. Glocker changed the name to *phoenicochroite*—from φοινίκεος, deep-red; and χρόα, colour—and this term was adopted by J. F. L. Hausmann, and J. D. Dana. W. Haidinger's term *phönicite* is more portable, so to speak, but it is too much like phenacite for use. R. Hermann's analysis corresponds with **lead oxybischromate,** $3PbO.2CrO_3$, $PbO.2PbCrO_4$, or $Pb_3Cr_2O_9$. W. E. Dawson gave $4PbO.3CrO_3$ for a variety obtained from Pretoria, Transvaal. Analyses of the artificial chromate in agreement with this were reported by C. Lüdeking, R. Weinland and F. Paul, and M. Lachaud and C. Lepierre. A. Drevermann obtained it together with the normal chromate by the slow mixing by diffusion of soln. of potassium chromate and lead nitrate. R. Weinland and F. Paul obtained it by the action of sodium chromate soln. on a hot soln. of lead hydroxychlorate. A. C. Becquerel obtained it by electrolysis, through a connecting capillary tube, of soln. of potassium dichromate and plumbate; by the electrocapillary action of the same two soln. separated by a collodion or paper partition; by the long continued action of a soln. of potassium chromate on chalk previously boiled with a conc. soln. of lead nitrate; and by the action for several years of a Pt–Pb-couple on a conc. soln. of chromic chloride and china clay. N. S. Manross, and M. Lachaud and C. Lepierre obtained it by heating at a red-heat a mixture of lead chromate and molten sodium chloride; S. Meunier, by the action of a soln. of potassium dichromate on galena; and C. Lüdeking, by allowing a soln. of lead chromate in conc. potash-lye to stand for some months exposed to air. F. M. Jäger and H. C. Germs observed no sign of this compound in their study of the system $PbO–PbCrO_4$; nor was A. J. Cox more successful in his study of the system: $PbO–CrO_3–H_2O$. J. F. G. Hicks, however, said that he obtained it from fused mixtures of lead oxide and chromate in a molten equimolar mixture of potassium and sodium nitrates. According to R. Hermann, melanochroite is coloured hyacinth-red or cochineal-red, and it becomes lemon-yellow on exposure to air. It occurs in massive, and also in tabular crystals thought to be rhombic. The sp. gr. is 3·0 to 3·5, and the hardness 5·75. A. Drevermann described it as forming rhombic plates coloured like potassium ferricyanide; A. C. Becquerel, as orange-red, doubly refracting needles; and N. S. Manross, as deep red, hexagonal prisms. M. Lachaud and C. Lepierre said that the red, rhombic crystals have a sp. gr. 5·81; A. Drevermann found that the salt does not dissolve as readily as the normal chromate in a soln. of potassium hydroxide. Conc. nitric acid changes it into chrome-yellow.

M. Gröger reported **ammonium lead chromate,** $(NH_4)_2Pb(CrO_4)_2$, by dropping 50 c.c. of a cold, sat. soln. of ammonium chromate into 10 c.c. of a conc. soln. of lead acetate, and allowing the voluminous, yellow, amorphous precipitate to stand for some weeks in contact with the mother-liquor. M. Lachaud and C. Lepierre obtained microscopic, hexagonal plates of **lithium lead chromate,** $Li_2Pb(CrO_4)_2$, by heating freshly precipitated lead chromate with a very conc., neutral soln. of lithium chromate for 8 hrs. in a sealed tube at 140°; and by melting lead chromate with lithium nitrate when some lead oxychromate is formed at the same time. A basic salt could not be prepared. Normal **sodium lead chromate,** $Na_2Pb(CrO_4)_2$, was obtained in a similar way. The yellow prisms or plates are soluble in water. By heating lead chromate, lead oxychromate and sodium chromate in molten sodium nitrate, orange, microscopic prisms of **sodium lead dioxybischromate,** $2PbO.Na_2Pb(CrO_4)_2$, are produced. M. Barre obtained **potassium lead chromate,** $K_2Pb(CrO_4)_2$, from soln. of potassium chromate and lead chromate; L. Bourgeois, and M. Lachaud and C. Lepierre, obtained it by heating lead chromate, or a mixture of lead chromate and potassium chromate in molten potassium nitrate for 3 hrs.; and M. Gröger, by shaking 50 c.c. of an almost sat. soln. of potassium chromate with 10 c.c. of a conc. soln. of potassium acetate—with lead nitrate some hydroxynitrate is formed as well. The yellow, hexagonal plates melt in a crucible over the bunsen flame. The salt is insoluble in water and in alcohol; and with dil. acids, lead chromate is formed. According to M. Barre, the salt is decomposed by water, potassium chromate passing into soln., but with the following proportions of potassium chromate in 100 parts of water, the salt is insoluble at the temp. indicated:

	10°	27·5°	37·5°	50°	70°	100°
K_2CrO_4 . . .	8·950	8·077	7·629	7·150	6·145	4·940

C. Immerwahr said that the electrode potential of lead against lead chromate suspended in $2M$-K_2CrO_4 is 0·536 volt. M. Gröger said that the *monohydrate,* $K_2Pb(CrO_4)_2.H_2O$, is formed by the action of lead chromate on potassium acetate soln., or of potassium chromate on lead acetate soln. M. Lachaud and C. Lepierre obtained **potassium lead dioxychromate,** $2PbO.K_2Pb(CrO_4)_2$, in orange prisms by the method used for the sodium salt. M. Lachaud and C. Lepierre also prepared **barium, strontium, and calcium lead chromates** by the method used for the alkali salts. For **copper lead chromate,** *vide infra,* vauquelinite. A. Breithaupt described a mineral from Berezoff, Urals, as occurring in orange-yellow crystals—possibly **zinc lead chromate.** The mineral was called **jossoite.** Its sp. gr. is 5·2; and its hardness 3.

S. H. C. Briggs[26] heated 3·5 grms. of antimony oxychloride, $2SbOCl.Sb_2O_3$, with 6 grms. of chromic trioxide and 6 c.c. of water in a sealed tube for 4 hrs. at 200°. The tube contained a straw-yellow sublimate, and an orange-yellow deposit in spherical, crystalline aggregates, insoluble in water, and slowly soluble in nitric acid—*vide supra*, antimony chromite. The composition approximated *antimony tetroxybischromate*, $3SbO_2.2CrO_3$, or $Sb_3O_4(CrO_4)_2$. Although normal **bismuth chromate,** $Bi_2(CrO_4)_3$, has not been prepared, K. Preis and B. Rayman obtained what they regarded as **potassium bismuth chromate,** $4K_2CrO_4.Bi_2(CrO_4)_3$, by mixing a soln. of 2 mols of bismuth nitrate with a soln. of 9 mols of potassium chromate. The precipitate is non-crystalline. J. Milbauer obtained only a 6·3 per cent. conversion to chromate when a mixture of bismuth oxide or carbonate and chromic oxide was heated to 480° in oxygen at 12 atm. press. A number of basic salts has been reported, with $Bi_2O_3 : CrO_3 : H_2O = 3:1:0$; $3:2:0$; $1:1:0$; $1:2:1$; $5:11:6$; and $3:7:0$. Of these, A. J. Cox recognized only the 1 : 2 : 1-compound—the 1 : 4 : 1-compound may be a basic dichromate. The 5 : 11 : 6-compound, reported by M. M. P. Muir to be formed by the protracted boiling of the 1 : 4 : 1-compound with dil. nitric acid, is considered by A. J. Cox to be an impure 1 : 2 : 1-compound; and a similar remark applies to the 3 : 7 : 0-compound reported by M. M. P. Muir to be formed by heating the 1 : 4 : 1-compound with conc. nitric acid. The other basic salts are supposed to be impure 1 : 2 : 1 or 1 : 4 : 1-compounds or mixtures of these. The results of A. J. Cox's examination of the ternary system: Bi_2O_3–CrO_3–H_2O at 25° are summarized in Fig. 64. If the soln. at 25° has a smaller conc. than 7·80 mols of CrO_3 per litre, the 1 : 4 : 1-compound is hydrolyzed and it passes into the 1 : 2 : 1-compound, which is stable even when the soln. is almost pure water. S. H. C. Briggs did not succeed in making a bismuth chromate—*vide supra*, bismuth chromite.

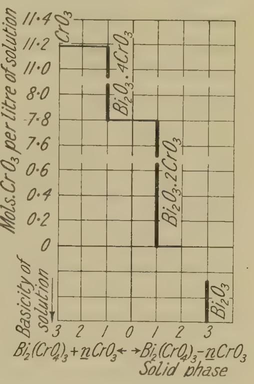


FIG. 64.—Equilibrium Diagram of the Ternary System: Bi_2O_3–CrO_3–H_2O at 25°.

W. Schmid reported the 3 : 1 : 0-compound or $3Bi_2O_3.CrO_3$, which may be **bismuthyl orthochromate,** $(BiO)_6CrO_6$. It is said to be formed by boiling bismuthyl hydroxide with a conc. soln. of potassium chromate. The heavy, pale orange powder is washed with boiling water. It can be heated to redness without decomposition. J. Löwe prepared the 3 : 2 : 0-compound—possibly **bismuthyl paradichromate,** $(BiO)_3{\equiv}CrO{-}O{-}CrO{\equiv}(BiO)_3$—by pouring a soln. of bismuth nitrate, containing as little free nitric acid as possible, into an excess of a soln. of potassium chromate, and washing the product with hot water. W. Schmid obtained it by heating the 1 : 2 : 1-compound with molten potassium nitrate, and leaching the soluble salts from the cold product with water; and M. M. P. Muir, by boiling the 5 : 11 : 6- or the 3 : 7 : 0-compound with potash-lye. A. J. Cox regarded this product as a mixture of bismuth oxide and the 1 : 2 : 1-compound. J. Löwe said that the lemon-yellow, micro-crystalline powder contains only one per cent. of water when dried at 110°. It can be heated to redness without melting or without decomposition. It is insoluble in cold or hot water; it is freely soluble in an excess of dil. hydrochloric or nitric acid, but if the acid be not in excess, the 1 : 2 : 1-compound is formed. When boiled with dil. soda-lye, it forms a bright red basic salt. "Bismuth chromate," said A. Naumann, "is insoluble in acetone."

M. M. P. Muir reported the 1 : 1 : 0-compound, **bismuthyl chromate,** $Bi_2O_3.CrO_3$, or $(BiO)_2CrO_4$, to be formed by treating a soln. of bismuth nitrate with an excess of potassium chromate or dichromate, and, after the addition of a few drops of nitric acid, boiling the mixture for a few hours until it is transformed into a red powder. The product is washed with hot water, and dried at 100°. It is also obtained by boiling the 1 : 2 : 1-compound with a soln. of potassium dichromate and hydroxide. The vermilion-coloured powder consists of microscopic needles. It does not decompose when heated in a crucible over the bunsen-flame, but when strongly heated it becomes dark brown; it is insoluble in water, soluble in dil. hydrochloric acid, but not so soluble in dil. nitric or sulphuric acid. Boiling soda-lye converts part of it into the 3 : 1 : 0-compound, and part is dissolved.

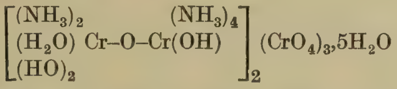
J. Löwe poured a nearly neutral soln. of bismuth nitrate into an excess of a warm soln. of potassium dichromate and boiled the mixture for some time. The product, washed with water and dried at 140°, consisted of $Bi_2O_3.2CrO_3$, or $Bi_2O_3.2CrO_3$, that is, *bismuthyl dichromate*, $(BiO)_2Cr_2O_7$, or **bismuth hydroxychromate,** $Bi(OH)CrO_4$. M. M. P. Muir, W. Schmid, and K. Preis and B. Rayman also prepared this salt. R. W. Pearson obtained a product by a similar process, but regarded it as the 1 : 1 : 0-compound. F. Nolle also prepared a similar salt. A. J. Cox showed that this compound is produced by the hydrolysis of the 1 : 4 : 0-compound—Fig. 64. At 25°, the salt is stable in the presence of water containing not less than 0·00001 mol of chromic acid per litre. J. Löwe obtained it by the action of mineral acids on the 1 : 1 : 0-compound; W. Schmid, by boiling bismuthyl hydroxide with an excess of a soln. of chromic acid; and M. M. P. Muir, by the action of dil. nitric acid on the 1 : 4 : 1-compound. J. Löwe, W. Schmid, and A. J. Cox supposed the salt to be anhydrous; and M. M. P. Muir, hydrated. The anhydrous salt consists of minute, orange-yellow scales, which decompose at a red-heat; and are insoluble in hot or cold water, but soluble in dil. mineral acids.

M. M. P. Muir prepared the 1 : 4 : 1 compound—*bismuth hydroxydichromate*, $Bi_2O_3.4CrO_3.H_2O$, or else **bismuthyl quaterochromate,** $BiO.O.CrO_2.O.CrO_2.O.CrO_2.O.CrO_2.O.BiO$, without combined water—by boiling the 1 : 1 : 0-compound with a little conc. nitric acid. A. J. Cox obtained it by the action of chromic acid on bismuth oxide provided the soln. contains at least 7·8 mols of CrO_3 per litre at 25°—Fig. 64. The salt is washed with a similar soln. of chromic acid. The salt prepared by A. J. Cox was not hydrated; M. M. P. Muir's product was said to be the monohydrate when dried at 100°; but A. J. Cox said that it was not completely dried. M. M. P. Muir found that the water is expelled at 200°–250°. The small ruby-red crystals are monoclinic prisms which decompose when strongly heated, forming a reddish vapour and a green residue. It is insoluble in hot and cold water; but it dissolves freely in mineral acids; with conc. hydrochloric acid, chlorine is evolved. It forms a pale orange product when boiled for a long time with dil. nitric acid.

The **vanadium chromates** have been discussed in connection with the chromium vanadates. According to C. W. Blomstrand,[27] an aq. soln. of columbium oxychloride gives a yellow, granular precipitate of **columbium chromate** when it is treated with potassium chromate.

The so-called **chromium chromates** have been discussed in connection with the oxides Cr_5O_9, or $2Cr_2O_3.CrO_3$; Cr_8O_{15}, or $3Cr_2O_3.2CrO_3$; CrO_2, or $Cr_2O_3.CrO_3$; Cr_4O_9, or $Cr_2O_3.2CrO_3$; Cr_5O_{12}, or $Cr_2O_3.3CrO_3$; and Cr_6O_{12}, or $Cr_2O_3.4CrO_3$. H. J. S. King prepared **chromic hydroxypentamminochromate,** $[Cr(NH_3)_5(OH)]CrO_4$, by the action of the chloride of the base in ammoniacal soln. on ammonium chromate. O. T. Christensen[28] prepared **chromic nitritopentamminochromate,** $[Cr(NH_3)_5(NO_2)]CrO_4$, by treating the corresponding chloride with a cold, sat. soln. of potassium chromate. The salt forms small, yellow crystals, sparingly soluble in water; and they explode like gunpowder when heated. A. Hiendlmayr prepared **chromic fluopentamminochromate,** $[Cr(NH_3)_5F]CrO_4$, by the action of potassium chromate on a soln. of the chloride of the series. S. M. Jörgensen prepared **chromic chloropentamminochromate,** $[Cr(NH_3)_5Cl]CrO_4$, by treating the corresponding chloride or nitrate with potassium chromate, and, after filtration, washing the product with cold water. The microscopic, rhombic plates are soluble in water. P. T. Cleve obtained **chromic aquo-**

chlorotetramminochromate, $[Cr(NH_3)_4)H_2O)Cl]CrO_4$, from a soln. of the corresponding chloride by the addition of potassium chromate. The brownish-black powder decomposes when heated. S. M. Jörgensen obtained **chromic bromopentamminochromate,** $[Cr(NH_3)_5Br]CrO_4$, from a cold sat. soln. of the nitrate by the addition of N-K_2CrO_4. The brownish-red product forms the chloride when treated with hydrochloric acid. He also prepared **chromic oxyaquotrihydroxyhexamminochromate,** $[Cr_2(O_4H_5)(NH_3)_6]_2(CrO_4)_3.5H_2O$, or



$$\left[\begin{array}{l}(NH_3)_2 \qquad\qquad (NH_3)_4\\ (H_2O)\ Cr{-}O{-}Cr(OH)\\ (HO)_2\end{array}\right]_2 (CrO_4)_3,5H_2O$$

by the action of potassium chromate in excess on a soln. of the chloride. The microscopic, reddish-brown, rhombic plates are sparingly soluble in water. P. Pfeiffer and W. Vorster prepared **chromic hexaethylenediaminohexahydroxychromate,** $[Cr_4(OH)_6(en)_6](CrO_4)_3.5H_2O$, from a soln. of the chloride and a conc. soln. of potassium chromate. The brownish-red compound is decomposed by a prolonged boiling with water. W. J. Sell prepared **chromic hexacarbamidochromate,** $[Cr(CON_2H_4)_6](CrO_4)_3.4H_2O$.

J. J. Berzelius[29] obtained a basic **molybdenum chromate** by adding potassium chromate to a soln. of molybdenum chloride; and another basic salt as a precipitate by adding ammonia to a soln. of the dichromate. The pale yellow soln. when spontaneously evaporated furnishes white or yellowish-white acicular or scaly crystals which are efflorescent. A. Atterberg prepared **molybdous tetrabromochromate,** $[Mo_3Br_4]CrO_4$. If a soln. of molybdous tetrabromodihydroxide in alkali-lye be treated with potassium dichromate, no precipitate is formed; but if an acid, say acetic acid, be also added, the soln. becomes dark red, and a dark purple-brown powder is precipitated. The compound decomposes when heated. It is insoluble in dil. acids, but soluble in hot, conc. hydrochloric acid. It is decomposed by alkali-lye; and it is insoluble or sparingly soluble in soln. of alkali chromates. For **tungsten chromates,** see chromium tungstates.

According to H. Moser, and J. J. Berzelius, potassium chromate gives an ochre-yellow precipitate with uranyl nitrate; and C. F. Rammelsberg obtained a precipitate with uranium tetrachloride and potassium chromate—*vide supra,* uranium chromite; while J. F. John observed that a soln. of yellow uranic carbonate in chromic acid deposits red, cubic and dendritic crystals, which fuse with partial decomposition at a red-heat. According to N. A. Orloff, a sat. soln. of uranium trioxide in chromic acid, yields, on evaporation, yellow needles of normal **uranyl chromate,** $(UO_2)CrO_4.3H_2O$. At 15°, 100 parts of water dissolve 7·52 parts of the *trihydrate* forming a pure yellow soln., which, on evaporation at 100°, gives an amorphous, brown mass, soluble in water to a brown soln. Uranyl chromate dissolves slowly in alcohol at the ordinary temp.; this soln. decomposes on boiling, also when exposed to the action of sunlight, with the separation of a brown precipitate. The filtrate from this precipitate when evaporated to dryness yields an amorphous, brown mass, partially soluble in water; it probably consists of a mixture of uranyl chromate and chromous uranate. According to J. Formanek, the *henahydrate,* $(UO_2)CrO_4.11H_2O$, obtained by dissolving the hydroxide in an aq. soln. of chromic acid and concentrating the filtered soln. on the water-bath, crystallizes from boiling water in yellow needles, effloresces on exposure to the air, and loses the whole of its water at 200°; only silver, lead, mercurous, and bismuth salts produce precipitates in its aq. soln. In precipitating chromic acid as mercurous chromate, in presence of uranium salts, the mercurous nitrate employed must be free from oxides of nitrogen, and the soln. must be slightly acidic; otherwise some of the uranium salt is also precipitated. J. Aloy gave −6·3 Cals. for the heat of soln. of a mol of this salt in 1000–2500 mols of water at 18°–20°. According to N. A. Orloff, when potassium chromate is added to an aq. soln. of uranyl chromate, the basic salt, yellow **uranyl oxybischromate,** $UO_3.2UO_2CrO_4.8H_2O$, or

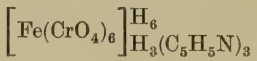
$(UO_2)_3O(CrO_4)_2.8H_2O$, is formed; and if uranyl acetate is similarly treated, **uranyl oxychromate,** $UO_3.UO_2CrO_4.6H_2O$, or $(UO_2)_2O(CrO_4).6H_2O$, is formed. He added that the formation of the basic salts indicates that in soln. uranyl chromate behaves like a mixture of uranic and chromic acids. S. H. C. Briggs obtained a complex, $2UO_3.3CrO_3.2Py$, with pyridine.

J. Formanek observed that yellow plates of **ammonium uranyl chromate,** $(NH_4)_2CrO_4.2(UO_2)CrO_4.6H_2O$, are produced by mixing a soln. of a mol of uranyl nitrate with a soln. of a mol of ammonium chromate, and evaporating the liquor over sulphuric acid; the same salt is obtained by treating ammonium uranate with a warm, conc. soln. of chromic acid, and evaporating the filtered liquid over sulphuric acid. The yellow, monoclinic crystals of the *hexahydrate* have the axial ratios $a:b:c=0{\cdot}8016:1:1{\cdot}0196$, and $\beta=72°\ 31'$. The salt is partially decomposed by boiling water. In some cases, probably owing to a variation of temp., orange-red crystals of a *trihydrate* were formed. J. Formanek obtained **potassium uranyl chromate,** $K_2CrO_4.2UO_2CrO_4.6H_2O$, by a process analogous to that employed for the ammonium salt. The axial ratios of the yellow, monoclinic plates or prisms were $a:b:c=0{\cdot}7566:1:0{\cdot}9714$, and $\beta=107°\ 22'$. The salt is soluble in acidulated water, and it is decomposed by boiling water. J. Wiesner reported a number of complex potassium salts are formed by precipitation from mixtures of uranyl nitrate and potassium chromate, *viz.*, $K_4(UO_2)_3(CrO_4)_5.7H_2O$; $K_6(UO_2)_4(CrO_4)_7.7H_2O$; $K_2(UO_2).(CrO_4)_2.H_2O$; and $K_2Cr_2O_7.3(UO_2)CrO_4.14H_2O$. J. Formanek, H. Bürger, and E. Rimbach obtained yellow crystals of **sodium uranyl chromate,** $Na_2CrO_4.2UO_2CrO_4.10H_2O$, by a process analogous to that employed for the ammonium salt. The salt is freely soluble in water, without decomposition. J. Formanek obtained **silver uranyl chromate** as a vermilion precipitate by treating a soln. of uranyl chromate with silver nitrate. Unlike J. Formanek, B. Szilard was unable to detect any decomposition of silver uranyl chromate in light even after several days' exposure. J. Formanek prepared **mercurous uranyl chromate** in a similar manner; so also **lead uranyl chromate;** and **bismuth uranyl chromate.**

According to J. F. John,[30] an aq. soln. of chromic acid slowly dissolves manganese with the evolution of hydrogen; manganous oxide and carbonate are also dissolved by the acid forming, presumably, soln. of **manganous chromate.** The soln. has an acidic reaction and a pungent, metallic taste, and after repeated evaporation it deposits nearly all the manganese in a higher state of oxidation. T. Thomson said that potassium chromate or dichromate does not give a precipitate with manganous salts immediately, but after some time, especially with the chromate, a brownish-black precipitate is produced. According to U. Antony and U. Paoli, if excess of alkali hydroxide be added to a soln. containing a chromium and a manganese salt in the proportion $Mn:8Cr(O=16)$, no precipitate is obtained, but the liquid is coloured emerald green and must be regarded as a colloidal soln. of the hydroxides of chromium and manganese, since this behaviour is exhibited only when the salts are present in exactly the above ratio. Chromium being tervalent and having both an acid and basic function, whilst manganese is bivalent and decidedly metallic in its properties, it is inferred that they exist in this soln. in the form of a salt, an electrolyte, which must be either a manganous chromite or polychromite. When this liquid is exposed to the air, or, better, when oxygen is passed through it, it quickly turns brown but remains free from precipitate. The element undergoing the oxidation is the manganese which becomes quadrivalent; the *rôles* of the two elements thus become interchanged and a more or less basic chromium manganite is formed. The chromium hydroxide now begins to undergo oxidation and the amount of chromate formed in the soln. increases until about 60 per cent. of the chromium has been converted. Continued action of oxygen has now no further effect on the liquid which, after a time, deposits a dark precipitate of constant composition, the proportion $Mn:Cr$ having the value $1:3$; when this compound is treated with cold dil. sulphuric acid, the chromium dissolves as sulphate whilst the manganese remains in soln. as the hydrate of manganese dioxide.

If now to this liquid is added an alkaline soln. of chromium hydroxide, the latter undergoes immediate and complete oxidation. U. Antony and U. Paoli also measured the speed of the oxidation. R. Warington observed that manganous salts are coloured yellowish-brown by potassium chromate, and in time a dark brown precipitate is formed; which, with dil. soln., may be crystalline **manganous oxychromate,** $MnO.MnCrO_4.2H_2O$, in agreement with the analyses of R. Warington, and H. Reinsch. C. Freese obtained a similar salt from a boiling soln. of manganous sulphate and potassium chromate; and A. J. Fairrie, using manganous chloride, obtained what he regarded as $3Mn_2O_3.Cr_2O_3.3CrO_3.6H_2O$. E. Schulze was unable to obtain a manganous chromate from a cold soln. of manganous carbonate and chromic acid. C. Freese said that the oxychromate loses half its water at 180° and the remainder at 300°; P. Grouvelle, that the salt is slightly soluble in water; and R. Warington, that with potash-lye it furnishes potassium chromate; with hydrochloric acid it gives chlorine; and dissolves in sulphuric or nitric acid forming an orange-yellow liquid. E. Donath described the use of manganese chromate as a pigment *chrome-brown.* C. Hensgen prepared **ammonium manganous chromate,** $(NH_4)_2CrO_4.2MnCrO_4.4H_2O$, as a precipitate from a mixed soln. of manganous and ammonium sulphates. It can be crystallized from a soln. of chromic acid. The bluish-black crystals resemble iodine. It decomposes at 200°, and if the salt be rapidly heated, a slight explosion occurs. The corresponding **ammonium manganous trischromate,** $K_2CrO_4.2MnCrO_4.2H_2O$, was obtained in a similar way, and by varying the proportions of the component salts used in the preparation, intermediate compounds are formed. M. Gröger obtained **potassium manganous bischromate,** $K_2CrO_4.MnCrO_4.2H_2O$, from $4N$-K_2CrO_4 mixed with an equal vol. of N-$MnCl_2$. F. Breinl and J. Klaudy supposed the salt to be monohydrated. According to M. Gröger, the salt is decomposed by water, with the separation of a brown precipitate. It gives an orange-red soln. with sulphuric acid. No definite compound was obtained by using a greater excess of the chromate soln., and with boiling soln. chromium manganite is formed.

It is scarcely to be expected that **ferrous chromate** could be prepared in aq. soln. because of the strongly oxidizing properties of the chromates and chromic acid; L. N. Vauquelin [31] obtained a yellowish-brown precipitate on adding potassium chromate to a soln. of ferrous sulphate. The precipitate gave up no chromic acid to alkali-lye, and formed a green soln. with nitric acid. C. Lepierre found that the product of the action is a basic complex ferric salt—*vide infra.* Neither A. Maus, nor C. W. Eliot and F. H. Storer, were able to prepare normal **ferric chromate.** According to A. Maus, if a soln. of a ferric salt be treated with alkali chromate, a brown powder is formed which is resolved by water into soluble chromic acid, and insoluble ferric oxide. A brown soln. is obtained when hydrated ferric oxide is digested with chromic acid. The soln. is not rendered turbid by dilution with water, or by boiling; and, on evaporation, it yields a brown mass soluble in water and in alcohol. L. A. Wels found the magnetic susceptibility of **potassium ferric chromate,** $K[Fe(CrO_4)_2].2H_2O$, to be $39{\cdot}44\times10^{-6}$ mass unit. The brown product obtained by the action of potassium chromate on a soln. of a ferric salt was found by V. Kletzinsky, and C. W. Eliot and F. H. Storer to have the composition of **ferryl chromate,** $(FeO)_2CrO_4$. L. Blanc also prepared the basic chromate. S. H. C. Briggs obtained ferric oxybischromate, $2Fe_2O_3.4CrO_3.H_2O$, or $(FeCrO_4)_2O.\frac{1}{2}H_2O$, by treating 5 grms. of ferric chloride as in the case of the aluminium salt. The shining black crystals were mixed with a highly coloured, more basic substance. According to C. Hensgen, **ammonium ferric chromate,** $(NH_4)_2CrO_4.Fe_2(CrO_4)_3.4H_2O$, is obtained when the precipitate, produced by mixing conc. soln. of ammonium chromate and ferric chloride, is dissolved in hydrochloric acid, and the soln. slowly evaporated. The dark red, leafy, crystalline mass is rapidly washed with cold water, or with alcohol and ether. It decomposes when heated, or when left in contact with water. C. Lepierre obtained the same salt in red crystals by evaporating a cold soln. of ferric chloride and ammonium dichromate. C. Hensgen obtained **potassium ferric chromate,** $K_2CrO_4.Fe_2(CrO_4)_3.4H_2O$, by a process analogous to that used for the ammonium salt; it is decomposed slowly by water. According to R. Weinland and E. Mergenthaler, when a mixed soln. of ferric nitrate, chromic acid, and ammonia is heated on a water-bath, carmine red, insoluble ammonium ferric chromate, $NH_4[Fe(CrO_4)_2]$, separates; and likewise, under analogous conditions, potassium ferric chromate, $K[Fe(CrO_4)_2].2H_2O$, as a sparingly soluble, dark orange-red, microcrystalline powder. With pyridine under similar conditions, there is formed **pyridine ferric chromate,**



$$\left[Fe(CrO_4)_6\right]\begin{matrix}H_6\\H_3(C_5H_5N)_3\end{matrix}$$

C. Lepierre found that C. Hensgen's salt is produced by the action of ferric chloride with a large excess of potassium dichromate; if ferric chloride be in excess, potassium chlorochromate is one of the products; if neither salt is in excess, ruby-red crystals of the basic salt *potassium ferric oxyseptieschromate,* $2K_2CrO_4.Fe_2(CrO_4)_3.FeO(CrO_4)_2.7H_2O$, are formed; and if the one soln. is allowed to diffuse into the other, anhydrous crystals of *potassium ferric trioxysexieschromate,* $3K_2CrO_4.Fe_2O_3.Fe_2(CrO_4)_3$, are produced. A sat. soln. of potassium chromate when added to an excess of a sat. soln. of ferric chloride yields ruby-red hexagonal crystals of *potassium ferric dioxyundecieschromate,* $4K_2CrO_4.2Fe_2(CrO_4)_3.(FeO)_2CrO_4$; with an excess of chromate, an orange-yellow precipitate of *potassium ferric trioxynovieschromate,* $6K_2CrO_4.Fe_2O_3.Fe_2(CrO_4)_3.nH_2O$, is formed—*hexahydrate,* if washed with alcohol, and the *decahydrate* if washed with water; with only a slight excess of ferric salt, *potassium ferric pentoxydecieschromate,* $6K_2CrO_4.Fe_2O_3(FeO)_2CrO_4.Fe_2(CrO_4)_3$. In all cases, in hot soln., the products are mixtures. If a soln. of 6 mols of ferrous sulphate and 2 mols of potassium chromate be allowed to react at 0°, *potassium ferric enneadecaoxybischromate,* $3K_2O.6Fe_2O_3.2CrO_3$, is formed. It is washed with water, alcohol, and ether at 0°; when moist, it is brown, and when dried, black. After drying in the air, it retains about 30 per cent. of water. The action of ferrous sulphate on potassium chromate at higher temp. yields only basic ferric sulphates. The action of excess of potassium chromate on ferrous sulphate yields a yellowish-brown, micro-crystalline precipitate of *potassium ferric enneaoxyquaterchromate,* $4K_2CrO_4.3Fe_2O_3$, which retains 22·7 per cent. of water when dried in air. If ammonium ferrous sulphate be employed, the precipitate is *potassium ferric pentadecaoxydecieschromate,* $7K_2CrO_4.Fe_2(CrO_4)_3.5Fe_2O_3$. If ferric chloride be employed with sodium chromate, *sodium ferric oxyquinquieschromate,* $4Na_2CrO_4.6Fe_2O_3.(FeO)_2CrO_4$, is formed; and with ammonium chromate, *ammonium ferric pentadecaoxysexieschromate,* $6(NH_4)_2CrO_4.5Fe_2O_3$. If ammonium and sodium dichromates are employed, immediate oxidation occurs without forming basic chromates. It is not to be supposed that these basic salts are all chemical individuals.

Potassium chromate with soln. of cobalt salts gives a reddish-brown precipitate which is probably a basic salt. F. J. Malaguti and M. Sarzeau[32] represented it as **cobaltous dioxychromate,** $2CoO.CoCrO_4.4H_2O$, or $3CoO.CrO_3.4H_2O$. S. H. C. Briggs obtained **cobaltous chromate,** $CoCrO_4$, by heating a soln. of the carbonate in chromic acid in a sealed tube at 260° for several hrs. The greyish-black crystals are readily soluble in dil. nitric acid. The *dihydrate,* $CoCrO_4.2H_2O$, is obtained in bronze coloured prisms or leaflets, when soln. of cobalt acetate and potassium chromate are mixed. The salt is always contaminated with some double chromate. F. de Boer studied the X-ray spectrum. N. Parravano and A. Pasta obtained yellow needles of *cobaltous bisethylenediaminochromate,* $CoCrO_4.2C_2H_4(NH_2)_2$. C. Freese said that **cobaltous oxychromate,** $CrO.CoCrO_4.2H_2O$, appears as a reddish-brown precipitate when boiling soln. of a cobaltous salt and potassium chromate are mixed. One mol. of water is expelled at about 220°, and the other at about 300°. The dehydrated salt slowly takes up water again from moisture. M. Gröger dissolved cobalt carbonate in the cold soln. of an eq. amount of N-CrO_3. The filtrate is evaporated, and when the residue is taken up with water there remains the brownish-black *monohydrate* of cobaltous oxychromate. F. J. Malaguti and M. Sarzeau found that when the dioxychromate is treated with ammonia it forms orange-yellow needles, and an amorphous, ruby-red product.

O. W. Gibbs and F. A. Genth, and C. D. Braun treated cobaltic hexamminonitrate with potassium chromate and obtained a yellow precipitate of **cobaltic hexamminochromate,** $[Co(NH_3)_6]_2(CrO_4)_3.5H_2O$. O. W. Gibbs and F. A. Genth,

C. D. Braun, and T. Klobb also prepared **cobaltic hexamminochlorochromate,** $[Co(NH_3)_6]Cl(CrO_4)$ with $1\frac{2}{3}$ and with 3 mols. of water. G. Vortmann treated an aq. soln. of cobaltic chloroaquotetramminochloride with potassium dichromate and obtained **cobaltic octamminochromate,** $Co_2(NH_5)_8(CrO_4)_3.4H_2O$. The brown precipitate furnishes bronze brown plates of the *tetrahydrate* when recrystallized from dil. acetic acid. If potassium chromate be used as precipitant, the olive-green *decahydrate* is formed. According to S. H. C. Briggs, if a cobaltic diaquotetrammino-salt is added to a large excess of neutral sodium chromate, dark chocolate-brown cobaltic octamminochromate, $Co_2(CrO_4)_3.8NH_3.2\frac{1}{2}H_2O$, is formed, and this furnishes the monohydrate, if kept in vacuo. A. Hiendlmayr prepared **cobaltic fluopentamminochromate,** $[Co(NH_3)_5F]CrO_4$, by the action of potassium chromate on a soln. of the fluoride of the series. O. W. Gibbs prepared **cobaltic nitritopentamminochromate,** $[Co(NH_3)_5NO_2]CrO_4.H_2O$, as a yellow precipitate by adding potassium chromate to the corresponding nitrate. J. N. Brönsted and A. Petersen found its molar solubility at 20° to be $S=0{\cdot}000258$ and in the presence of various salts of molar conc. C,

	C	0·02	0·05	0·10	0·20	0·50	1·0
S	H.COOK	$0{\cdot}0_3361$	$0{\cdot}0_3481$	$0{\cdot}0_3636$	$0{\cdot}0_3816$	$0{\cdot}0_21212$	$0{\cdot}0_21787$
	H.COONa	$0{\cdot}0_3323$	$0{\cdot}0_3410$	$0{\cdot}0_3558$	$0{\cdot}0_3746$	$0{\cdot}0_21131$	$0{\cdot}0_21729$
	NaCl	—	$0{\cdot}0_3425$	$0{\cdot}0_3565$	$0{\cdot}0_3785$	—	—
	KCl	$0{\cdot}0_3371$	$0{\cdot}0_3520$	$0{\cdot}0_3690$	$0{\cdot}0_3887$	—	—
	$KClO_3$	$0{\cdot}0_3332$	$0{\cdot}0_3421$	$0{\cdot}0_3570$	—	—	—
	$NaClO_3$	$0{\cdot}0_3318$	$0{\cdot}0_3417$	$0{\cdot}0_3561$	—	—	—
	KNO_3	$0{\cdot}0_3345$	$0{\cdot}0_3444$	$0{\cdot}0_3588$	—	—	—
	$NaNO_3$	$0{\cdot}0_3344$	$0{\cdot}0_3442$	$0{\cdot}0_3577$	—	—	—
	$MgSO_4$	$0{\cdot}0_362$	$0{\cdot}0_3908$	$0{\cdot}0_21237$	$0{\cdot}0_21804$	—	$0{\cdot}0_25120$

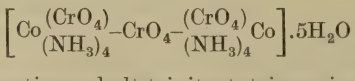
They also studied *cobaltic isothiocyanatopentamminochromate,* $[Co(NH_3)_5SCy]CrO_4$; and *cobaltic tetrathiocyanatodiamminochromates*; P. R. Ray prepared **cobaltic thiosulphatopentamminochromate,** $[Co(NH_3)_5(S_2O_3)]_2CrO_4$, by adding potassium chromate to the corresponding chloride. S. M. Jörgensen obtained, in an analogous manner, yellow, microscopic needles of **cobaltic cis-dinitritotetramminochromate,** $[Co(NH_3)_4(NO_2)_2]_2CrO_4$, and O. W. Gibbs, **cobaltic trans-dinitritotetramminochromate.** S. M. Jörgensen likewise obtained **cobaltic nitratopentamminochromate,** $[Co(NH_3)_5NO_3]CrO_4$, in ochre-yellow or brick-red octahedral crystals; also brick-red, microscopic crystals of **cobaltic chloropentamminochromate,** $[Co(NH_3)_5Cl]CrO_4$; and likewise greyish-brown, rosetted needles of **cobaltic chloroaquotetramminochromate,** $[Co(NH_3)_4(H_2O)Cl]CrO_4$; and brown, six-rayed aggregates of **cobaltic bromopentamminochromate,** $[Co(NH_3)_5Br]CrO_4$.

S. H. C. Briggs added a soln. of a cobaltic diaquotetrammino-salt to a large excess of an alkali chromate and obtained a series of alkali bischromatotetramminocobaltiates, $M'[Co(CrO_4)_2(NH_3)_4]$. A green form corresponds with the trans-configuration, and a brown form with the cis-configuration of the chromate radicles. The formation of the brown form is favoured by the presence of a large proportion of dichromate in the soln. The salts obtained were **lithium cis-bischromatotetramminocobaltiate,** $Li[Co(CrO_4)_2(NH_3)_4].1\frac{1}{2}H_2O$; **sodium trans-bischromatotetramminocobaltiate,** $Na[Co(CrO_4)_2(NH_3)_4]$, as a green, microcrystalline powder; and the corresponding **sodium cis-bischromatocobaltiate,** $Na[Co(CrO_4)_2.(NH_3)_4].H_2O$, in greenish-brown crystals; and **potassium trans-bischromatotetramminocobaltiate,** $K[Co(CrO_4)_2(NH_3)_4]$. If magnesium chromate be employed, **magnesium cisbischromatotetramminocobaltiate,** $Mg[Co(CrO_4)_2(NH_3)_4]_2.2H_2O$, is formed in brown crystals, and also **magnesium trans-bischromatotetramminocobaltiate,** $Mg[Co(NH_3)_4(CrO_4)_2]_2.8H_2O$, which, when dehydrated in vacuo over sulphuric acid, gives the *hexahydrate.* The *octohydrate* is thought to be $Mg[Co(NH_3)_4(CrO_4)_2(H_2O)_2]_2.4H_2O$, in which the co-ordination number of the cobalt atom is eight. If a cobaltic diaquotetrammino-salt be added to a large excess of neutral ammonium chromate, dark reddish-brown crystals of **ammonium chromatopentamminobischromate,**

$(NH_4)_2[Co(CrO_4)(NH_3)_5](CrO_4)_2$, are formed. With sodium chromate, the octammine is formed as indicated above.

M. Gröger prepared ammonium **cobaltous oxyquaterochromate,** $(NH_4)_2CrO_4.CoO.3CoCrO_4.3H_2O$, by the action of 2 vols. of N-$CoCl_2$ on one vol. of N-$(NH_4)_2CrO_4$. On allowing the precipitate to stand in contact with the mother-liquor for some time, dark brownish-red microscopic crystals are formed. The composition is different if other proportions of the constituent salt soln. are mixed. S. H. C. Briggs prepared **ammonium cobaltous chromate,** $(NH_4)_2CrO_4.CoCrO_4.6H_2O$, in brownish-yellow prisms, by adding a soln. of 30 grms. ammonium chromate in 60 c.c. of water to a soln. of 40 grms. crystallized cobalt acetate in 120 c.c. of water and cooled by ice and salt. The salt can be kept for some days at 8°, but it gradually darkens in colour, and loses water; decomposition is rapid at 20°. M. Gröger prepared **ammonium cobaltous diamminoquaterochromate,** $(NH_4)_2CrO_4.3CoCrO_4.2NH_3.3H_2O$, from cobaltous chloride and ammonium chromate. The dark brown product is decomposed by water and by heat. M. Gröger prepared brown **potassium cobaltous chromate,** $K_2CrO_4.CoCrO_4.2H_2O$, from a soln. of one vol. of $3N$-$CrCl_2$ and 3 vols. of $3N$-K_2CrO_4; and the basic salt **potassium cobaltous oxyquaterochromate,** $K_2CrO_4.CoO.3CoCrO_4.3H_2O$, or $HO.Co.CrO_4.Co.KCrO_4(H_2O)$, by mixing 2 vols. of N-$CoCl_2$ and one vol. of N-K_2CrO_4; or one vol. of the former and 2 vols. of the latter. The dark reddish-brown product consists of microscopic crystals, which are soluble in cold, dil. sulphuric acid, and are decomposed by water forming cobaltous dioxychromate. S. H. C. Briggs prepared **cæsium cobaltous chromate,** $Cs_2CrO_4.CoCrO_4.6H_2O$, as a brown crystalline powder, by mixing 2 grms. of cæsium chromate in 6 c.c. of cold water with a soln. of 1·2 grms. of crystalline cobalt acetate cooled to about —5°.

S. H. C. Briggs prepared a series of **chromatocobaltammines**—*e.g.* **cobaltic chromatopentamminonitrate,** $[Co(NH_3)_5(CrO_4)]NO_3$, by the action of potassium chromate on the aquopentamminonitrate. The salt is moderately soluble in cold water, and the freshly prepared soln. is not precipitated by silver, barium, or lead salts, but precipitation occurs at once in the boiling soln. Similarly, cobalt aquopentamminochloride furnishes brownish-red crystals of **cobaltic chromatopentamminochloride,** $[Co(NH_3)_5(CrO_4)]Cl$. If the mother-liquor is heated to 50° and treated with more potassium chromate, on cooling, it furnishes yellowish-brown prisms of **cobaltic chloropentamminochromate,** $[Co(NH_3)_5Cl)]CrO_4.2\frac{1}{2}H_2O$. If cobaltic chromatopentamminochloride in water at 60° be treated with silver chromate, **cobaltic chromatopentamminochromate,** $[Co(NH_3)_5(CrO_4)]_2CrO_4.3H_2O$, is formed in scaly crystals the colour of silver chromate. P. R. Ray and P. V. Sarkar represented it as a dihydrate, and obtained it by the action of ammonium dichromate and aq. ammonia on freshly precipitated cobalt hydroxide. By treating cobaltic diaquotetramminonitrate with a dil. soln. of potassium chromate, **cobaltic chromatotetramminonitrate,** $[Co(NH_3)_4(CrO_4)_2]NO_3.\frac{1}{2}H_2O$, was formed as a dark reddish-brown crystalline mass, soluble in water; if an excess of potassium chromate is used, **cobaltic chromatotetramminochromate,** $[Co(NH_3)_4(CrO_4)_2]CrO_4.3H_2O$, is formed as a brown crystalline powder. The corresponding dichromate (*q.v.*) was also prepared. By treating cobalt diaquotetramminonitrate with a conc. soln. of potassium chromate, a greenish precipitate of **cobaltic trichromatotetrammine,** $[Co(NH_3)_4(CrO_4)_2]CrO_4.5H_2O$,



$$\left[Co\begin{matrix}(CrO_4)\\(NH_3)_4\end{matrix}-CrO_4-\begin{matrix}(CrO_4)\\(NH_3)_4\end{matrix}Co\right].5H_2O$$

was obtained; and by treating cobalt trinitratotriammine with a soln. of potassium chromate, **cobaltic hydroxychromatotriammine,** $[Co(NH_3)_3(OH)(CrO_4)_2].2H_2O$, was formed—for the dichromate, *vide infra.*

According to R. Tupputi,[33] a soln. of chromic acid dissolves nickel hydroxide or carbonate forming a yellow soln. which deposits a powder soluble in a large excess of the acid. The soln. deposits a non-deliquescent mass of red crystals, which, according to J. F. John, are resolved at a red-heat into chromic and nickel oxides. If the soln. be treated with nickel carbonate, or with alkali-lye, R. Tupputi observed that a reddish-yellow insoluble powder of a **nickel oxychromate** is deposited; and H. Stokes, and F. J. Malaguti and M. Sarzeau observed that a basic salt is deposited when a soln. of nickel sulphate is mixed with potassium chromate. C. Freese added that the yellowish-brown product is scarcely attacked by cold potash-lye, but all the chromium is extracted by boiling lye. F. J. Malaguti and M. Sarzeau represented its composition by $4NiO.CrO_3.6H_2O$; C. Freese, by $3NiO.CrO_3.3H_2O$; and E. A. Schmidt obtained precipitates ranging from $3NiO.CrO_3.6H_2O$ to $2NiO.CrO_3.6H_2O$ by varying the conc. of the soln. employed. S. H. C. Briggs said that while nickel chromate is insoluble in water, it is not precipitated from nickel salt soln., and it must therefore be polymerized. It is formed by heating nickel carbonate and a soln. of chromic acid in a sealed tube at 260°. The black crystals of **nickel chromate,** $NiCrO_4$, are washed with water, alcohol, and ether. They are insoluble in hot dil. nitric acid, and are slowly attacked by conc. nitric acid or aqua regia. G. L. Clark found that **nickel hexamminochromate,** $Ni(NH_3)_6CrO_4$, has a vap. press. of 760 mm. at 408°.

S. H. C. Briggs obtained **ammonium nickel chromate,** $(NH_4)_2CrO_4.NiCrO_4.6H_2O$, by adding a soln. of ammonium chromate to a soln. of a nickel salt; and M. Gröger obtained it by adding $3N$-$(NH_4)_2CrO_4$ to half its vol. of N-$NiCl_2$, and allowing the mixture to stand for some time. The green crystals can be recrystallized from water at 40° without change. G. L. Clark studied the relations between the at. vol. and the stability. S. H. C. Briggs showed that when treated with ammonia, **ammonium nickel diamminochromate,** $(NH_4)_2CrO_4.NiCrO_4.2NH_3$, is formed. The product loses water and ammonia when it is heated, and it decomposes suddenly between 200° and 300°. M. Gröger obtained the basic salt, **ammonium nickel dihydroxyquaterchromate,** $3(NH_4)_2CrO_4.Ni(OH)_2.NiCrO_4$, from a mixture of a cold, sat. soln. of ammonium chromate with a fifth of its vol. of $3N$-$NiCl_2$. The yellowish-brown crystals are stable in air; they are decomposed by water with the separation of a basic nickel chromate; and form with water a yellowish-green soln. which when evaporated at a low temp. yield ammonium chromate, and ammonium nickel chromate. M. Gröger mixed $3N$-Na_2CrO_4 with half its vol. of N-$NiCrO_4$ and obtained a brown, amorphous precipitate, probably a basic sodium nickel chromate; and by mixing $3N$-K_2CrO_4 with half its vol. of N-$NiCrO_4$, a reddish-brown precipitate is formed which, when allowed to stand under its mother-liquor, becomes crystalline **potassium nickel chromate,** $K_2CrO_4.NiCrO_4.2H_2O$. This *dihydrate* is stable in air, and loses no water on the water-bath. It is decomposed by water with the separation of a basic salt. S. H. C. Briggs obtained the *hexahydrate* by adding 8 grms. of potassium chromate in 14 c.c. of water to 8 grms. of nickel acetate in 27 c.c. of water at —6°. The yellowish-green crystals dissolve in water with decomposition. The hexahydrate forms isomorphous mixtures with the corresponding sulphate. S. H. C. Briggs also prepared **rubidium nickel chromate,** $Rb_2CrO_4.NiCrO_4.6H_2O$; and **cæsium nickel chromate,** $Cs_2CrO_4.NiCrO_4.6H_2O$, in an analogous way. Both salts are decomposed by water.

The normal chromates of the platinum metals have not been prepared. According to T. Thomson,[34] a soln. of hydrochloroplatinic acid, when treated with potassium chromate furnishes a dark red precipitate containing potassium chloroplatinate. P. T. Cleve, and G. B. Buckton found that an ammoniacal soln. of platinous tetramminodichromate furnishes a yellow powder consisting of microscopic tablets of **platinous tetramminochromate,** $[Pt(NH_3)_4]CrO_4$. The same salt is formed by precipitation from a soln. of platinous chloride by potassium chromate. P. T. Cleve prepared **platinic dinitratotetramminochromate,** $[Pt(NH_3)_4(NO_3)_2]CrO_4$, by treating the corresponding chloride with potassium chromate and drying the product at 100°. The lemon-yellow product detonates sharply when heated; it is insoluble in water. He also prepared **platinic dichlorotetramminochromate,** $[Pt(NH_3)_4Cl_2]CrO_4$, in an analogous manner from the corresponding nitrate. So also with **platinic hydroxysulphatotetramminochromate,** $[Pt(NH_3)_4(OH)(SO_4)]CrO_4.2H_2O$; and with **platinic hydroxychlorotetramminochromate,** $[Pt(NH_3)_4(OH)Cl]CrO_4$. S. G. Hedin prepared **platinic sulphatotetrapyridinochromate,** $[Pt(C_5H_5N)_4(SO_4)]CrO_4.6H_2O$; and C. Enebuske, **platinic chromatobisethylsulphide,** $Pt\{(C_2H_5)_2S\}_2CrO_4$.

References.

[1] L. N. Vauquelin, *Ann. Chim. Phys.*, (1), **70**. 70, 1809 ; J. B. Richter, *Ueber die neueren Gegenstände der Chymie*, Breslau, **10**. 30, 1802 ; *Gehlen's Journ.*, **5**. 351, 1905 ; M. Groger, *Zeit. anorg. Chem.*, **36**. 412, 1908 ; H. Moser, *Chemische Abhandhung über das Chrom*, Wien, 1824 ; *Schweigger's Journ.*, **42**. 99, 1824 ; E. Maumené, *Bull. Soc. Chim.*, (3), **7**. 174, 1892 ; E. Jäger and G. Krüss, *Ber.*, **22**. 2030, 1889 ; C. Paal and G. Brünjes, *ib.*, **47**. 2211, 1914 ; A. Naumann, *ib.*, **37**. 4328, 1904 ; A. Maus, *Pogg. Ann.*, **9**. 127, 1827 ; **11**. 83, 1827 ; W. Müller, *ib.*, **127**. 404, 1866 ; Y. T. Gerasimoff, *Trans. Inst. Pure Chem. Reagents*, 6, 1927 ; A. Naumann and A. Rücker, *Journ. prakt. Chem.*, (2), **74**. 249, 1906 ; H. Hirzel, *Zeit. Pharm.*, **4**. 22, 1852 ; W. C. Ball, *Proc. Chem. Soc.*, **24**. 135, 1908 ; F. A. H. Schreinemakers, *Chem. Weekbl.*, **1**. 395, 1905 ; *Zeit. phys. Chem.*, **55**. 71, 1906 ; E. C. Franklin, *Amer. Chem. Journ.*, **20**. 826, 1898 ; F. W. Clarke, *Amer. Journ. Science*, (3), **14**. 281, 1877 ; H. G. F. Schröder, *Dichtigkeitsmessungen*, Heidelberg, 1873 ; *Liebig's Ann.*, **172**. 278, 1874 ; **174**. 249, 1874 ; S. Darby, *ib.*, **63**. 205, 1848 ; *Journ. Chem. Soc.*, **1**. 24, 1849 ; J. C. G. de Marignac, *Ann. Chim. Phys.*, (5), **8**. 418, 1876 ; *Arch. Sciences Genève*, (2), **55**. 113, 1876 ; M. S. Sherrill, *Journ. Amer. Chem. Soc.*, **29**. 1641, 1907 ; C. Watkins and H. C. Jones, *ib.*, **37**. 2626, 1915 ; K. F. Slotte, *Wied. Ann.*, **14**. 13, 1881 ; G. N. Wyrouboff, *Bull. Soc. Min.*, **2**. 170, 1879 ; **4**. 120, 1881 ; **3**. 77, 1890 ; J. W. Retgers, *Zeit. phys. Chem.*, **8**. 40, 1891 ; N. de Kolossowsky, *Journ. Chim. Phys.*, **22**. 225, 1925 ; P. Sabatier, *Compt. Rend.*, **103**. 267, 1886 ; F. Morges, *ib.*, **86**. 1443, 1878 ; M. Berthelot, *ib.*, **96**. 542, 1883 ; *Ann. Chim. Phys.*, (6), **1**. 92, 101, 1884 ; (5), **17**. 133, 1879 ; *Thermochimie*, Paris, **1**. 282, 1897 ; E. Kopp, *Chem. News*, **11**. 16, 1864 ; T. Ishikawa, *Bull. Japan. Chem. Soc.*, **1**. 139, 1926 ; E. Herlinger, *Zeit. Kryst.*, **42**. 454, 1925 ; J. J. Pohl, *Sitzber. Akad. Wien*, **6**. 592, 1851 ; J. Schabus, *ib.*, **5**. 369, 1850 ; *Bestimmung der Krystallgestalten in chemischen Laboratorien erzeugter Produkte*, Wien, 110, 1855 ; *Pogg. Ann.*, **116**. 429, 1862 ; C. F. Rammelsberg, *Handbuch der krystallographisch-physikalischen Chemie*, Leipzig, **1**. 587, 1881 ; *Pogg. Ann.*, **118**. 158, 1862 ; D. Brewster, *Phil. Mag.*, (4), **24**. 441, 1862 ; J. H. Gladstone, *Journ. Chem. Soc.*, **10**. 79, 1858 ; S. Araki, *Mem. Coll. Kyoto*, **8**. 213, 1925 ; I. Plotnikoff and M. Karshulin, *Zeit. Physik*, **38**. 502, 1926 ; H. Stamm, *Ueber die Löslichkeit von Ammonsalzen und Alkalisalzen in wässerigen Ammoniak*, Halle, 1926 ; M. G. Mellon, *Journ. Phys. Chem.*, **33**. 1931, 1929.

[2] G. C. Gmelin, *Schweigger's Journ.*, **43**. 110, 1825 ; C. F. Rammelsberg, *Pogg. Ann.*, **126**. 311, 1866 ; L. Schulerud, *Journ. prakt. Chem.*, (2), **19**. 37, 1879 ; J. W. Retgers, *Zeit. phys. Chem.*, **8**. 53, 1891 ; F. A. H. Schreinemakers, *ib.*, **55**. 71, 1906 ; *Chem. Weekbl.*, **2**. 633, 1905 ; F. Mylius and R. Funk, *Abh. Phys. Tech. Reichsanst.*, **3**. 456, 1900 ; *Ber.*, **30**. 1718, 1897 ; F. Mylius and J. von Wrochem, *ib.*, **30**. 1718, 1897 ; G. Tammann, *Bull. Acad. St. Petersburg*, (4), **35**. 9, 1887 ; *Zeit. phys. Chem.*, **2**. 44, 1888 ; P. P. von Weimarn, *Zeit. Koll.*, **9**. 25, 1911 ; A. Heydweiller, *Ann. Physik*, (4), **37**. 739, 1912 ; (4), **41**. 499, 1913 ; C. Watkins and H. C. Jones, *Journ. Amer. Chem. Soc.*, **37**. 2626, 1916 ; W. Kohlrausch, *Sitzber. Akad. Berlin*, 90, 1897 ; H. Traube, *Neues Jahrb. Min.*, ii, 58, 1892 ; i, 171, 1894 ; *Zeit. Physik*, **22**. 138, 1894 ; **24**. 168, 1895.

[3] F. Mylius and R. Funk, *Abh. Phys. Tech. Reichsanst.*, **3**. 456, 1900 ; *Ber.*, **30**. 1718, 1897 ; **33**. 3686, 1900 ; H. Salkowsky, *ib.*, **34**. 1947, 1901 ; A. Naumann, *ib.*, **37**. 4329, 1904 ; V. Rosiczky, *Zeit. Kryst.*, **45**. 473, 1909 ; F. A. H. Schreinemakers, *Chem. Weekbl.*, **2**. 211, 1905 ; *Zeit. phys. Chem.*, **55**. 93, 1906 ; J. Traube and W. von Behren, *ib.*, **138**. 85, 1928 ; J. W. Retgers, *ib.*, **8**. 47, 1891 ; T. W. Richards and R. C. Wells, *ib.*, **43**. 471, 1903 ; T. W. Richards and J. B. Churchhill, *ib.*, **28**. 314, 1899 ; T. W. Richards and G. L. Kelley, *Proc. Amer. Acad.*, **47**. 171, 1911 ; *Journ. Amer. Chem. Soc.*, **33**. 847, 1911 ; T. W. Richards and W. B. Meldrum, *ib.*, **43**. 1543, 1921 ; J. L. R. Morgan and E. Schramm, *ib.*, **35**. 1845, 1913 ; H. Ollivier, *Compt. Rend.*, **186**. 1001, 1928 ; C. A. L. de Bruyn, *Rec. Trav. Chim. Pays-Bas*, **11**. 156, 1892 ; *Zeit. phys. Chem.*, **10**. 783, 1892 ; A. Heydweiller, *Ann. Physik*, (4), **37**. 739, 1912 ; I. Takeuchi, *Mem. Coll. Kyoto*, **1**. 253, 1915 ; Y. Osaka and R. Yoshida, *ib.*, **6**. 49, 1922 ; *Journ. Japan. Chem. Soc.*, **43**. 12, 1922 ; Z. Zeltner, in H. Landolt and R. Börnstein, *Physikalisch-chemische Tabellen*, Berlin, 671, 1923 ; R. Hollmann, *Ann. Physik*, (4), **6**. 74, 1901 ; M. R. Nayer, H. E. Watson and J. J. Sudborough, *Journ. Indian Inst. Science*, **7**. 53, 1924 ; M. de K. Thompson, Y. C. Hsu, R. R. Ridgway, C. A. Norton and G. G. Kearful, *Trans. Amer. Electrochem. Soc.*, **46**. 37, 1924 ; L. Kahlenberg and W. J. Trautmann, *ib.*, **39**. 377, 1921 ; A. B. J. Jouve and A. Helbronner, *Brit. Pat. No.* 177174, 203709, 204290, 1922 ; I. Stscherbakoff, *Zeit. Elektrochem.*, **31**. 360, 1925 ; N. de Kolossowsky, *Journ. Chim. Phys.*, **22**. 225, 1925 ; P. Düllberg, *Zeit. phys. Chem.*, **45** 129, 1903 ; H. Stamm, *Ueber die Löslichkeit von Ammonsalzen und Alkalisalzen in wässerigen Ammoniak*, Halle, 1926 ; E. Flach, *Kaliumchromat und Natriumchromat, ihre Fähigkeit zur Mischkristall- und Doppelsalzbildung und ihre Beziehungen zu den entsprechenden Sulfaten*, Leipzig, 1912 ; *Neues Jahrb. Min.*, i, 212, 1913 ; J. J. Coleman, *Phil. Mag.*, (5), **23**. 1, 1887 ; W. Kohlrausch, *Sitzber. Akad. Berlin*, 90, 1897 ; H. Traube, *Neues Jahrb. Min.*, ii, 58, 1892 ; i, 171, 1894 ; *Zeit.*

Kryst., **22**. 138, 1894; **24**. 168, 1895; I. Traube, *Ber.*, **24**. 3078, 1891; H, Kopp, *Liebig's Ann.*, **42**. 99, 1842; M. Berthelot, *Thermochimie*, Paris, **1**. 282, 1897; *Compt. Rend.*, **87**. 574, 1878; **96**. 542, 1883; *Ann. Chim. Phys.*, (5), **17**. 133, 1879; (6), **1**. 92, 101, 1884; J. C. G. de Marignac, *ib.*, (5), **8**. 418, 1876; *Arch. Sciences Genève*, (2), **55**. 113, 1876; G. N. Wyrouboff, *Bull. Soc. Min.*, **2**. 177, 1879; **3**. 76, 1880; **5**. 160, 1882; L. Delhaye, *ib.*, **41**. 80, 1918; G. Tammann, *Bull. Acad. St. Petersburg*, (4), **35**. 9, 1887; *Zeit. phys. Chem.*, **2**. 44, 1888; *Kristallisieren und Schmelzen*, Leipzig, 262, 1903; D. Gernez, *Compt. Rend.*, **84**. 771, 1887; F. Morges, *ib.*, **86**. 1443, 1878; L. J. Simon, *ib.*, **178**. 1606, 1924; H. Lescoeur, *ib.*, **103**. 1262, 1886; *Sur la dissociation des hydrates salins et des composés analogues*, Lille, 1888; J. Zehenter, *Monatsh.*, **18**. 50, 1897; J. Thomsen, *Thermochemische Untersuchungen*, Leipzig, **1**. 255, 1882; *Journ. prakt. Chem.*, (2), **17**. 165, 1878; S. W. Johnson, *Journ. prakt. Chem.*, (1), **62**. 261, 1854; J. F. John, *Schweigger's Journ.*, **3**. 378, 1811; H. Moser, *Chemische Abhandhung über das Chrom*, Wien, 1824; *Schweigger's Journ.*, **42**. 99, 1824; H. J. Brooke, *Ann. Phil.*, **22**. 287, 1823; T. Thomson, *ib.*, **16**. 321, 1820; E. W. Washburn and E. R. Smith, *Bur. Standards Journ. Research*, **2**. 787, 1929; K. F. Slotte, *Wied. Ann.*, **14**. 13, 1881; F. W. Clarke, *Amer. Journ. Science*, (3), **14**. 281, 1877; W. G. Mixter, *ib.*, (4), **26**. 125, 1908; W. A. Tilden, *Journ. Chem. Soc.*, **45**. 268, 1884; H. C. Jones and H. P. Bassett, *Amer. Chem. Journ.*, **34**. 316, 1905; C. Watkins and H. C. Jones, *Journ. Amer. Chem. Soc.*, **37**. 2626, 1915; F. E. Brown and J. E. Snyder, *ib.*, **47**. 2671, 1925; J. L. R. Morgan and H. K. Benson, *Journ. Amer. Chem. Soc.*, **29**. 1168, 1907; *Zeit. anorg. Chem.*, **55**. 263, 1907; A. Scherbatscheff, *Bull. Soc. Chim.*, (2), **21**. 413, 1874; R. Lenz, *Mem. Acad. St. Petersburg*, (7), **26**. 3, 1879; (7), **30**. 64, 1882; E. Herlinger, *Zeit. Kryst.*, **62**. 454, 1925; J. d'Ans and J. Löffler, *Ber.*, **63**. B, 1446, 1930; A. Berthoud, *Helvetica Chim. Acta*, **13**. 17, 1930; B. Neumann and C. Exssner, *Zeit. angew. Chem.*, **43**. 440, 1930; I. Gerasimoff, *Zeit. anorg. Chem.*, **187**. 321, 1930; C. Leenhardt, *Recherches expérimentales sur la vitesse de cristallisation des sels hydratés*, Paris, 1908.

[4] T. Thomson, *Ann. Phil.*, **16**. 321, 1820; R. T. Thomson, *Chem. News*, **52**. 59, 1885; J. von Liebig and F. Wöhler, *Pogg. Ann.*, **24**. 171, 1832; E. Mitscherlich, *ib.*, **18**. 168, 1830; R. F. Marchand, *ib.*, **45**. 594, 1838; P. Kremers, *ib.*, **96**. 63, 1855; P. Groth, *ib.*, **133**. 216, 1868; C. F. Rammelsberg, *ib.*, **91**. 321, 1854; K. Stammer, *ib.*, **82**. 135, 1851; W. Müller, *ib.*, **127**. 404, 1866; A. E. Nordenskjöld and G. Lindström, *ib.*, **136**. 314, 1869; H. Rose, *ib.*, **52**. 585, 1844; F. Rüdorff, **122**. 337, 1864; *Ber.*, **21**. 3047, 1888; V. Kletzinsky, *Zeit. Chem.*, (2), **2**. 127, 1866; A. A. Hayes, *Amer. Journ. Science*, (1), **20**. 409, 1831; A. Hettich and A. Schleede, *Zeit. Physik*, **50**. 249, 1928; N. J. Berlin, *Journ. prakt. Chem.*, (1), **38**. 143, 1848; C. von Hauer, *ib.*, (1), **83**. 359, 1861; (1), **103**. 114, 1868; J. Jacobson, *Liebig's Ann.*, **40**. 265, 1841; *Journ. prakt. Chem.*, (1), **33**. 467, 1841; F. Stolba, *ib.*, (1), **97**. 503, 1865; E. Fleischer, *ib.*, (2), **5**. 312, 1872; E. Schweizer, *ib.*, (1), **65**. 173, 1855; *Repert. Pharm.*, **3**. 212, 1854; H. de Sénarmont, *Ann. Chim. Phys.*, (3), **33**. 413, 1851; H. V. Regnault, *ib.*, (3), **1**. 166, 1841; H. Becquerel, *ib.*, (5), **30**. 5, 1883; L. C. de Coppet, *ib.*, (4), **25**. 536, 1872; *Zeit. phys. Chem.*, **22**. 239, 1897; P. Walden, *ib.*, **1**. 546, 1887; **2**. 70, 1888; E. Pietsch, A. Kotowsky and G. Berend, *Zeit. phys. Chem.*, **5**. B, 1, 1929; E. Kopp, *Chem. News*, **11**. 16, 1864; H. Kopp, *Liebig's Ann. Suppl.*, **3**. 296, 1865; *Liebig's Ann.*, **36**. 1, 1840; H. Schiff, *ib.*, **110**. 74, 1859; E. Viterbi and G. Krausz, *Gazz. Chim. Ital.*, **57**. 690, 1927; W. Spring, *Ber.*, **15**. 1940, 1882; *Bull. Acad. Belg.*, (3), **4**. 201, 1882; S. F. Schemtschuschny, *Journ. Russ. Phys. Chem. Soc.*, **38**. 1135, 1907; *Zeit. anorg. Chem.*, **57**. 267, 1908; R. Lorenz and W. Herz, *ib.*, **135**. 374, 1924; W. J. Grailich and V. von Lang, *Sitzber. Akad. Wien*, **27**. 21, 1857; H. Topsöe and C. Christiansen, *Ann. Chim. Phys.*, (5), **1**. 5, 1874; *Danske Selsks. Förh.*, (5), **9**. 57, 1873; J. W. Döbereiner, *Schweigger's Journ.*, **22**. 476, 1818; *Trommsdorff. Journ.*, **5**. 250, 1818; C. J. B. Karsten, *ib.*, **65**. 394, 1832; H. G. I. Schröder, *Dichtigkeitsmessungen*, Heidelberg, 1873; *Liebig's Ann.*, **174**. 449, 1874; L. Playfair and J. P. Joule, *Mem. Chem. Soc.*, **1**. 157, 1843; **2**. 401, 1845; H. le Chatelier, *Compt. Rend.*, **118**. 350, 1894; *Bull. Soc. Chim.*, (2), **47**. 300, 1887; E. Montignie, *ib.*, (4), **45**. 492, 1929; J. B. Senderens, *ib.*, (3), **6**. 804, 1891; (3), **7**. 514, 1892; H. Moser, *Chemische Abhandlung über das Chrom*, Wien, 1824; *Schweigger's Journ.*, **42**. 99, 1824; M. Alluard, *Compt. Rend.*, **59**. 500, 1864; P. Job, *ib.*, **186**. 1546, 1928; L. J. Simon, *ib.*, **178**. 1606, 1924; F. Morges, *ib.*, **86**. 1445, 1878; **87**. 15, 1878; F. M. Raoult, *ib.*, **87**. 169, 1878; P. Sabatier, *ib.*, **103**. 49, 267, 1886; *Journ. Phys.*, (2), **6**. 312, 1887; W. Kohlrausch, *Sitzber. Akad. Berlin*, 90, 1897; F. A. H. Schreinemakers, *Chem. Weekbl.*, **1**. 837, 1905; *Zeit. phys. Chem.*, **55**. 93, 1906; H. von Halban and K. Siedentopf, *ib.*, **100**. 208, 1922; R. Kollmann, *ib.*, **37**. 202, 1901; G. Tammann, *ib.*, **2**. 42, 1838; *Bull. Acad. St. Petersburg*, (4), **35**. 9, 1887; G. Tammann and A. Sworykin, *Zeit. anorg. Chem.*, **173**. 73, 1928; K. F. Slotte, *Wied. Ann.*, **14**. 18, 1881; H. Settegast, *ib.*, **7**. 242, 1879; O. Knoblauch, *ib.*, **43**. 750, 1891; M. Herz, *Zur Kenntnis der Löslichkeit von Mischkristallen*, Berlin, 1895; H. Faasch, *Ueber die spezifische Wärme von wässerigen Salzlösungen*, Rostock, 1911; T. Graham, *Phil. Trans.*, **140**. 1, 805, 1850; 483, 1851; *Journ. Chem. Soc.*, **3**. 60, 1851; *Phil. Mag.*, (3), **37**. 181, 254, 341, 1850; M. Berthelot, *Compt. Rend.*, **96**. 542, 1883; *Ann. Chim. Phys.*, (6), **1**. 92, 101, 1884; W. Bohlendorff, *Studien zur Absorptionsspectralanalyse* Erlangen, 1890; E. Flach, *Kaliumchromat und Natriumchromat, ihre Fähigkeit zur Mischkristall- und Doppelsalzbildung und ihre Beziehungen zu den entsprechenden Sulfaten*, Leipzig, 1912; *Neues Jahrb. Min.*, i, 212, 1913; J. M. Hiebendaal, *Onderzoek over eenige absorptie spectra*, Utrecht, 1873; J. L. Soret, *Arch. Sciences Genève*, (2), **61**. 322, 1878; A. Hare, *Phil. Mag.*, (6), **48**. 412, 1924; H. Steinmetz, *Zeit. phys. Chem.*, **52**. 449, 1905; P. Düllberg, *ib.*, **45**. 129, 1903; J. Obermiller, *ib.*, **109**. 145, 1924; G. Stadnikoff, *Koll. Zeit.*, **31**. 19, 1922; L. Kahlen-

berg and W. J. Trautmann, *Trans. Amer. Electrochem. Soc.*, **39**. 377, 1921 ; I. Bencowitz and H. T. Hotchkiss, *Journ. Phys. Chem.*, **30**. 643, 1926 ; I. Bencowitz, *ib.*, **29**. 1432, 1925 ; H. P. Cady and R. Taft, *ib.*, **29**. 1057, 1925 ; F. Göbel, *Bull. Soc. Nat. Moscow*, **9**. 312, 1836 ; *Journ. prakt. Chem.*, (1), **6**. 386, 1835 ; F. Flöttmann, *Zeit. anal. Chem.*, **73**. 1, 1928 ; *Ueber Löslichkeitsgleichgewichte*, Merburg, 1928 ; J. C. G. de Marignac, *Arch. Sciences Genève*, (2), **50**. 89, 1874 ; (2), **55**, 113, 1876 ; *Ann. Chim. Phys.*, (2), **8**. 418, 1876 ; P. Berthier, *ib.*, (3), **7**. 77, 1843 ; F. Tassaert, *ib.*, (1), **22**. 51, 1823 ; J. L. Lassaigne, *ib.*, (2), **14**. 299, 1820 ; A. Michel and L. Krafft, *ib.*, (3), **41**. 478, 1854 ; W. Ipatieff and B. A. Mouromtseff, *ib.*, **183**. 505, 1926 ; W. Ipatieff and A. Kisseleff, *Journ. Russ. Phys. Chem. Soc.*, **50**. 664, 686, 692, 698, 1926 ; A. Étard, *ib.*, (7), **2**. 550, 1894 ; *Compt. Rend.*, **85**. 444, 1897 ; **120**. 1058, 1895 ; E. Bouty, *ib.*, **98**. 140, 1884 ; F. Fouqué, *ib.*, **64**. 124, 1867 ; *Ann. Obs. Paris*, **9**. 172, 1868 ; J. J. Berzelius, *Lehrbuch der Chemie*, Dresden, **2**. ii, 495, 1826 ; G. Gore, *Proc. Roy. Soc.*, **20**. 441, 1872 ; **21**. 140, 1873 ; *Phil. Mag.*, (4), **29**. 541, 1865 ; F. Guthrie, *ib.*, (4), **49**. 18, 1875 ; (5), **17**. 470, 1884 ; S. Holker, *ib.*, (3), **27**. 213, 1845 ; J. A. Wilson, *Chem. Trade Journ.*, **6**. 92, 1890 ; *Zeit. angew. Chem.*, **3**. 187, 1890 ; M. M. Richter, *Zeit. anal. Chem.*, **21**. 204, 1882 ; G. T. Gerlach, *ib.*, **8**. 288, 1869 ; F. Mohr, *ib.*, **11**. 278, 1872 ; *Liebig's Ann.*, **185**. 289, 1877 ; T. V. Barker, *Journ. Chem. Soc.*, **89**. 1120, 1906 ; *Zeit. Kryst.*, **45**. 1, 1908 ; L. Meyer, *Ber.*, **6**. 101, 1873 ; K. Vierordt, *ib.*, **5**. 34, 1872 ; I. Traube, *ib.*, **24**. 3076, 1891 ; R. C. Woodcock, *Journ. Chem. Soc.*, **24**. 785, 1871 ; S. Glasstone, D. W. Dimond and E. C. Jones, *ib.*, **129**. 2935, 1926 ; J. W. Thomas, *ib.*, **33**. 367, 1878 ; F. Margueritte, *Journ. Pharm. Chim.*, (3), **27**. 21, 1855 ; F. Gorio, *Atti Soc. Modena*, **16**. 73, 1898 ; J. T. Cooper, *Ann. Phil.*, **20**. 77, 1824 ; H. J. Brooke, *ib.*, **22**. 210, 1823 ; I. Plotnikoff and M. Karshulin, *Zeit. Physik*, **38**. 502, 1926 ; J. Lundberg, *Zeit. anorg. Chem.*, **55**. 426, 1907 ; I. Koppel and E. Blumenthal, *ib.*, **53**. 249, 1907 ; W. Herz and F. Hiebenthal, *ib.*, **177**. 363, 1929 ; E. Groschuff, *ib.*, **58**. 102, 1908 ; O. Döpping, *Liebig's Ann.*, **46**. 172, 1843 ; K. Brückner, *Monatsh.*, **27**. 199, 1906 ; J. Zehenter, *ib.*, **18**. 51, 1897 ; J. A. Fleming and J. Dewar, *Proc. Roy. Soc.*, **61**. 380, 1897 ; R. Lenz, *Bull. Acad. St. Petersburg*, (5), **26**. 3, 1878 ; F. W. O. de Coninck, *Bull. Acad. Belg.*, 275, 1905 ; H. de Vries, *Rec. Trav. Chim. Pays-Bas*, **3**. 375, 1884 ; G. Meyer, *ib.*, **42**. 301, 1923 ; F. Grünbaum, *Zur Photometrie der Absorptionsspektren von Lösungen*, Berlin, 1903 ; *Ann. Physik*, (4), **12**. 1010, 1903 ; A. Heydweiller, *ib.*, (4), **30**. 873, 1909 ; (4), **41**. 499, 1913 ; T. L. Phipson, *Chem. News*, **4**. 125, 1861 ; H. M. Vernon, *ib.*, **66**. 104, 114, 141, 152, 1892 ; G. C. Gmelin, *Schweigger's Journ.*, **43**. 110, 1825 ; E. F. Anthon, *Repert. Pharm.*, (2), **9**. 346, 1837 ; *Journ. prakt. Chem.*, (1), **10**. 353, 1837 ; S. W. Johnson, *ib.*, (1), **62**. 261, 1854 ; H. Stamm, *Ueber die Löslichkeit von Ammonsalzen und Alkalisalzen in wässerigen Ammoniak*, Halle, 1926 ; I. Domeyko, *Elementos de mineralojia*, Santiago, 1879 ; A. Raimondi, *Minéraux de Perou*, Paris, 1878 ; *Bull. Soc. Min.*, **1**. 144, 1878 ; E. Mallard, *ib.*, **3**. 3, 1880 ; G. N. Wyrouboff, *ib.*, **2**. 98, 1879 ; W. B. Morehouse, *Phys. Rev.*, (2), **29**. 765, 1927 ; H. Baumhauer, *Zeit. deut. geol. Ges.*, **35**. 639, 1883 ; E. Maumené, *Bull. Soc. Chim.*, (3), **7**. 174, 1892 ; O. Lehmann, *Molekularphysik*, Leipzig, **1**. 172, 1888 ; *Zeit. Kryst.*, **5**. 613, 1881 ; L. Stibing, *ib.*, **41**. 611, 1906 ; B. Gossner, *ib.*, **39**. 155, 1904 ; A. Fock, *ib.*, **28**. 379, 1897 ; O. Schott, *ib.*, **5**. 613, 1881 ; *Beiträge zur Kenntnis der anorganischen Schmelzverbindungen*, Braunschweig, 1881 ; F. Rinne, *Neues Jahrb. Min.*, i, 171, 1900 ; H. Traube, *ib.*, ii, 58, 1892 ; i, 171, 1894 ; *Zeit. Kryst.*, **22**. 138, 1894 ; **24**. 168, 1895 ; W. Brendler, *ib.*, **58**. 445, 1923 ; A. Wesch, *Ueber Chromsäurederivate*, Freiburg i B., 16, 1909 ; E. H. Riesenfeld and A. Wesch, *Ber.*, **41**. 3536, 1908 ; A. Naumann, **37**. 3601, 1904 ; **42**. 3790, 1909 ; **47**. 1370, 1914 ; F. E. Neumann, *Pogg. Ann.*, **126**. 123, 1865 ; G. Magnus, *ib.*, **20**. 477, 1830 ; H. C. Jones and C. A. Jacobson, *Amer. Chem. Journ.*, **40**. 355, 1908 ; A. M. Clover and H. C. Jones, *ib.*, **43**. 187, 1910 ; H. C. Jones and W. W. Strong, *Phys. Zeit.*, **10**. 499, 1909 ; *A Study of Absorption Spectra*, Washington, D.C., 25, 1910 ; R. Marc and W. Wenk, *Zeit. phys. Chem.*, **68**. 104, 1909 ; E. Ramann and H. Sallinger, *ib.*, **98**. 103, 1921 ; J. L. Andreae, *ib.*, **76**. 491, 1911 ; A. Benrath and J. Weinoff, *ib.*, **77**. 257, 1911 ; J. Wagner, *ib.*, **5**. 31, 1890 ; M. Amadori, *Atti Accad. Lincei*, (5), **21**. i, 667, 1912 ; (5), **22**. i, 453, 609, 1912 ; F. Santi, *Boll. Chim. Faren*, **43**. 673, 1904 ; E. C. Franklin and C. A. Kraus, *Amer. Chem. Journ.*, **20**. 829, 1898 ; H. Hermann, M. Hosenfeld and N. Schönfeldt, *Wiss. Veröffent. Siemens-Konzern*, **5**. 119, 1926 ; E. Kochholm and N. Schönfeldt, *ib.*, **6**. 177, 1927 ; W. Eidmann, *Ein Beitrag zur Erkenntnis des Verhaltens chemischer Verbindungen in nichtwässrigen Lösungen*, Giessen, 1899 ; K. W. Floroff, *Koll. Zeit.*, **36**. 215, 1925 ; G. Baborovsky, *Zeit. Elektrochem.*, **11**. 465, 1905 ; A. des Cloizeaux, *Nouvelles recherches sur les propriétés des cristaux*, Paris, 1867 ; S. Araki, *Mem. Coll. Kyoto*, **8**. 213, 1925 ; A. Kailan, *Anz. Akad. Wien*, **61**. 161, 1924 ; L. R. Ingersoll, *Journ. Amer. Opt. Soc.*, **6**. 663, 1922 ; N. R. Dhar, *Journ. Indian Chem. Soc.*, **5**. 585, 1928 ; R. L. Datta and N. R. Dhar, *Journ. Amer. Chem. Soc.*, **38**. 1303, 1916 ; M. Neidle and T. C. Witt, *ib.*, **37**. 2360, 1915 ; **38**. 47, 1916 ; A. Cavazzi, *Gazz. Chim. Ital.*, **44**. i, 448, 1914 ; N. de Kolassowsky, *Journ. Chim. Phys.*, **22**. 225, 1925 ; E. Divers, *Phil. Trans.*, **163**. 359, 1873 ; C. Schaefer and M. Schubert, *Zeit. Physik*, **7**. 297, 1921 ; T. Ishikawa, *Bull. Japan. Chem. Soc.*, **1**. 139, 1926 ; A. C. Robertson, *Proc. Nat. Acad.*, **13**. 192, 1927 ; L. A. Welo, *Phil. Mag.*, (7), **6**. 481, 1928 ; A. E. Lindh, *Ark. Mat. Fys.*, **18**. 14, 1924 ; *Compt. Rend.*, **172**. 1175, 1921 ; **175**. 25, 1922 ; *Zeit. Physik*, **6**. 303, 1921 ; **31**. 210, 1925 ; D. Coster, *ib.*, **25**. 83, 1924 ; O. Stelling, *ib.*, **50**. 506, 626, 1928 ; W. Schneider, *ib.*, **51**. 263, 1928 ; H. Fromherz, *Zeit. phys. Chem.*, **1**. B, 301, 1928 ; R. F. Reed and S. C. Horning, *Journ. Phys. Chem.*, **33**. 136, 1929 ; W. R. Hodgkinson and J. Young, *B.A. Rep.*, 676, 1892 ; G. Grasser and T. Nagahama, *Journ. Agric. Hokkaido Univ.*, **24**. 1, 1928 ; D. F. Smith and F. A. Hartgen, *Fuel*, **8**. 302, 1929 ; D. M. Yost, *Phil. Mag.*, (7), **8**. 845, 1929 ; J. W. Retgers, *Zeit. phys. Chem.*, **8**. 47, 1891 ; H. E. Buckley, *Zeit. Kryst.*, **75**. 15, 1930 ; A. C. Robertson, *Proc. Nat. Acad.*, **13**. 192, 1927 ;

M. Bobtelsky, *Zeit. anorg. Chem.*, **189**. 196, 1930; A. M. Taylor, *Trans. Faraday Soc.*, **25**. 856, 1929; E. Pietsch, A. Kotowsky and G. Berend, *Zeit. phys. Chem.*, **5**. B, 1, 1929; G. Jander and A. Winkel, *ib.*, **149**. 97, 1930; G. Jander, *Metallbörse*, **20**. 1855, 1930; W. von Behren and J. Traube, *Zeit. phys. Chem.*, **146**. 1, 1930; T. Aden, *Die Aenderungen der Absorptionsspektren im sichtbaren und ultravioletten Gebiet bei Aggregationen in Lösungen schwacher anorganischer Säuren und ihre Salze*, Göttingen, 1929; P. F. Gaehr, *Phys. Rev.*, (1), **32**. 476, 1911; N. R. Tawde and G. R. Paranjpe, *Indian Journ. Phys.*, **4**. 533, 1930; G. Gore, *Electrochemistry*, London, 96, 1906; K. Weber, *Arch. Kem. Farm.*, **4**. 113, 1930; *Zeit. Electrochem.*, **36**. 26, 1930.

[5] L. Grandeau, *Ann. Chim. Phys.*, (3), **67**. 227, 1863; J. Piccard, *Bull. Soc. Chim.*, (1), **5**. 254, 1863; *Journ. prakt. Chem.*, (1), **86**. 455, 1862; F. A. H. Schreinemakers and H. Filippo, *Chem. Weekbl.*, **3**. 157, 1906; J. W. Retgers, *Zeit. phys. Chem.*, **8**. 39, 1891; G. N. Wyrouboff, *Bull. Soc. Min.*, **4**. 129, 1881; T. V. Barker, *Journ. Chem. Soc.*, **89**. 1120, 1906; *Zeit. Kryst.*, **45**. 1, 1908.

[6] C. Chabrié, *Compt. Rend.*, **132**. 680, 1901; T. V. Barker, *Journ. Chem. Soc.*, **89**. 1120, 1906; *Zeit. Kryst.*, **45**. 1, 1908; F. R. Fraprie, *Amer. Journ. Science*, (4), **21**. 309, 1906; J. W. Retgers, *Zeit. phys. Chem.*, **8**. 46, 1891; F. A. H. Schreinemakers and D. J. Meijeringh, *Chem. Weekbl.*, **5**. 811, 1908.

[7] L. and P. Wöhler, *Zeit. phys. Chem.*, **62**. 445, 1908; J. Schulze, *Zeit. anorg. Chem.*, **10**. 150, 1895; S. H. C. Briggs, *ib.*, **56**. 253, 1908; *Journ. Chem. Soc.*, **83**. 394, 1902; **85**. 673, 1904; 242, 1929; G. Krüss and O. Unger, *Zeit. anorg. Chem.*, **8**. 455, 1895; M. Prud'homme, *Bull. Soc. Mulhouse*, **59**. 607, 1889; M. Prud'homme and F. Binder, *Bull. Soc. Chim.*, (2), **37**. 195, 1882; J. C. G. de Marignac, *ib.*, (2), **41**. 541, 1882; *Arch. Sciences Genève*, (3), **11**. 399, 1884; G. Brügelmann, *Ueber Krystallisation und physikalische Bindung*, Leipzig, 1884; *Ber.*, **15**. 1840, 1882; M. Rosenfeld, *ib.*, **12**. 958, 1879; **13**. 1473, 1880; G. C. Gmelin, *Schweigger's Journ.*, **43**. 110, 1825; G. Quincke, *Ann. Physik*, (6), **11**. 459. 1903; H. Kopp, *Liebig's Ann.*, **42**. 98, 1842; A. Knopp, *ib.*, **70**. 52, 1849; F. Dröge, *ib.*, **101**. 39, 1857; C. W. Juch, *Journ. prakt. Chem.*, (1), **29**. 204, 1843; T. Leykauf, *ib.*, (1), **22**. 448, 1841; A. Viefhaus, *ib.*, (1), **88**. 431, 1863; R. Böttger, *Beiträge zur Physik und Chemie*, Frankfurt a. M., **2**. 77, 1842; W. E. Garrigues, *Journ. Amer. Chem. Soc.*, **20**. 508, 1898; L. N. Vauquelin, *Ann. Chim. Phys.*, (1), **70**. 70, 1809; B. Skormin, *Ueber die basischen Chromate bezw. auch die chromsauren Kaliumdoppelsalze des Zink-, Cadmium-, Kupfer- und Quecksilberoxyds*, Berlin, 1896; F. J. Malaguti and M. Sarzeau, *ib.*, (3), **9**. 434, 1843; J. Persoz, *ib.*, (3), **25**. 283, 1849; *Compt. Rend.*, **53**. 71, 1861; C. Gerhardt, *Journ. pharm. Chim.*, (3), **12**. 57, 1847; M. Vuaflart, *ib.*, (2), **10**. 607, 1831; C. Freese, *Pogg. Ann.*, **140**. 242, 1870; A. Bensch, *ib.*, **55**. 97, 1842; H. Moser, *Chemische Abhandlung über das Chrom*, Wien, 1824; *Schweigger's Journ.*, **42**. 99, 1824; M. Gröger, *Sitzber. Akad. Wien*, **113**. 155, 1903; *Monatsh.*, **24**. 484, 1903; *Zeit. anorg. Chem.*, **58**. 420, 1908; L. Balbiano, *Atti Accad. Lincei*, (4), **4**. 597, 1888; *Gazz. Chim. Ital.*, **18**. 195, 1888; N. Parravano and A. Pasta, *ib.*, **37**. ii, 255, 1907; G. Gore, *Proc. Roy. Soc.*, **21**. 140, 1873; R. Otto, *Zeit. Chem.*, (2), **3**. 604, 1867; *Zeit. anal. Chem.*, **7**. 117, 1868; J. W. Slater, *Chem. Gaz.*, **11**. 329, 1853; M. C. Schuyten, *Bull. Acad. Belg.*, (3), **37**. 651, 1899; P. A. Bolley, *Schweiz. Polyt. Ztg.*, **2**. 18, 1857; *Polyt. Centr.*, 606, 1857; I. C. Zimmermann, *ib.*, **95**. 495, 1854; *Polyt. Centrh.*, **5**. 97, 1854; J. Stinde, *Dingler's Journ.*, **180**. 479, 1866; *Hamburger Gewerbeblatt*, 121, 1866; W. Grüne, *ib.*, **133**. 42, 1854; F. Rose, *Die Mineralfarben*, Leipzig, 270, 1916; J. G. Gentele, *Lehrbuch der Farbenfabrikation*, Braunschweig, **2**. 205, 1909; S. Tschelnitz, *Farbenchemie*, Wien, 56, 1857; G. Zerr and G. Rübencamp, *Handbuch der Farbenfabrikation*, Berlin, 345, 1909; London, 126, 1908; H. J. P. Venn and V. Edge, *Journ. Chem. Soc.*, 2142, 1928; N. W. Morse, *Journ. Phys. Chem.*, **34**. 1554, 1930.

[8] F. Wöhler and F. Rautenberg, *Liebig's Ann.*, **114**. 119, 1860; W. Muthmann, *Ber.*, **20**. 983, 1887.

[9] R. F. Carpenter, *Journ. Soc. Chem. Ind.*, **5**. 286, 1886; E. Ramann and H. Sallinger, *Zeit. phys. Chem.*, **98**. 103, 1921; R. Warington, *Phil. Mag.*, (3), **11**. 489, 1837; M. Storz, *Koll. Zeit.*, **45**. 231, 1928; M. S. Dunin and F. M. Schemjakin, *ib.*, **48**. 167, 1929; **39**. 50, 1926; B. Kisch, *ib.*, **49**. 154, 1929; S. Hedges and R. V. Henley, *Journ. Chem. Soc.*, 2714, 1928; C. Freese, *Pogg. Ann.*, **140**. 77, 1869; E. Mitscherlich, *ib.*, **12**. 141, 1828; B. M. Margosches, *Zeit. anorg. Chem.*, **41**. 68, 1904; **51**. 231, 1906; F. Köhler, *ib.*, **96**. 207, 1916; *Koll. Zeit.*, **19**. 65, 1916; E. Jäger and G. Krüss, *Ber.*, **22**. 2050, 1889; W. Autenrieth, *ib.*, **35**. 2057, 1902; J. Krutwig, *ib.*, **14**. 304, 1881; N. W. Fischer, *Kastner's Arch.*, **8**. 488, 1826; **9**. 351, 1826; *Pogg. Ann.*, **8**. 488, 1826; J. W. Retgers, *Zeit. phys. Chem.*, **8**. 52, 1891; F. Kohlrausch, *ib.*, **50**. 355, 1905; **64**. 129, 1908; R. Abegg and A. J. Cox, *ib.*, **46**. 1, 1904; R. Abegg and H. Schäfer, *Zeit. anorg. Chem.*, **45**. 293, 1905; H. Bechold, *Zeit. phys. Chem.*, **52**. 185, 1905; L. L. de Koninck and E. Nihoul, *Zeit. angew. Chem.*, **4**. 295, 1891; J. Milbauer, *Chem. Ztg.*, **40**. 587, 1916; A. Jaques, *Chem. News*, **96**. 77, 1907; R. E. Liesegang, *Zeit. phys. Chem.*, **88**. 1, 1914; *Zeit. angew. Chem.*, **35**. 345, 1922; *Koll. Zeit.*, **9**. 296, 1911; **38**. 151, 1926; *Naturwiss.*, **18**. 645, 1930; E. Hatschek, *ib.*, **8**. 196, 1911; **37**. 297, 1925; **38**. 151, 1926; Second Report on Colloid Chemistry, *B.A. Rep.*, 21, 1918; *Proc. Roy. Soc.*, **96**. A, 496, 1921; *Journ. Soc. Chem. Ind.*, **30**. 256, 1911; F. A. Gooch and L. H. Weed, *Zeit. anorg. Chem.*, **59**. 94, 1908; *Amer. Journ. Science*, (4), **26**. 85, 1908; A. A. Hayes, *ib.*, (2), **20**. 409, 1855; F. A. Gooch and R. S. Bosworth, *ib.*, **27**. 241, 1909; *Zeit. anorg. Chem.*, **62**. 68, 71, 1909; M. Gröger, *ib.*, **54**. 185, 1906; **58**. 412, 1908; G. S. Whitby, *ib.*, **67**. 107, 1910; G. P. Baxter, E. Mueller and M. A. Hines, *ib.*, **62**. 313, 1909; *Journ. Amer. Chem. Soc.*, **31**. 529, 1909; M. S. Sherrill and D. E. Russ, *ib.*, **29**. 1673, 1907; M. S. Sherrill, *ib.*, **29**. 1641,

1907; E. C. Franklin and C. A. Kraus, *Amer. Chem. Journ.*, **20**. 828, 1898; **21**. 1, 1899; S. J. Thugutt, *Kosmos*, **35**. 506, 1910; G. Meinecke, *Liebig's Ann.*, **261**. 339, 1891; T. R. Bolam and B. N. Desal, *Trans. Faraday Soc.*, **24**. 50, 1928; W. G. Young, *Analyst.*, **18**. 124, 1893; H. G. F. Schröder, *Dichtigkeitsmessungen*, Heidelberg, 1873; *Liebig's Ann.*, **172**. 298, 1874; **173**. 72, 1874; **174**. 249, 1874; A. Lottermoser, *Journ. Prakt. Chem.*, (2), **72**. 39, 1905; Chemische Fabrik von Heyden, *German Pat., D.R.P.* 166154, 1903; L. N. Vauquelin, *Ann. Chim. Phys.*, (1), **80**. 70, 1809; I. Guareschi, *Atti Accad. Torino*, **48**. 735, 1913; B. Guerini, *Volumétrie physico-chimique de précision avec les conductivités comme indicateurs*, Lausanne, 1922; O. Hähnel, *Gleichgewichtsstudien an heterogenen Systemen*, Berlin, 1910; H. Baubigny and G. Chavanne, *Compt. Rend.*, **136**. 1197, 1903; H. Topsöe, *Sitzber. Akad. Wien*, **66**. 18, 1872; W. Ostwald, *Koll. Zeit.*, 380, 1925; J. F. G. Hicks and W. A. Craig, *Journ. Phys. Chem.*, **26**. 563, 1922; F. Bush, *ib.*, **31**. 931, 1927; P. B. Ganguly, *ib.*, **31**. 481, 1927; E. R. Riegel and M. C. Reinhard, *ib.*, **31**. 713, 1927; H. N. Holmes, *Journ. Franklin Inst.*, **184**. 743, 1917; A. M. W. Williams and M. R. MacKenzie, *Journ. Chem. Soc.*, **117**. 844, 1920; P. Ray and J. Dasgupta, *Journ. Indian Chem. Soc.*, **5**. 519, 1928; T. R. Bolam and M. R. MacKenzie, *Trans. Faraday Soc.*, **22**. 151, 162, 1926; N. R. Dhar and A. C. Chatterji, *ib.*, **21**. 89, 1925; **23**. 23, 1927; *Journ. Soc. Chem. Ind.—Chem. Ind.*, **48**. 878, 1929; *Chem. News*, **121**. 253, 1920; *Journ. Phys. Chem.*, **28**. 41, 1924; *Zeit. anorg. Chem.*, **159**. 129, 186, 1926; L. N. Mukherjee and A. C. Chatterji, *Koll. Zeit.*, **50**. 147, 1930; N. R. Dhar and S. Ghosh, *Zeit. anorg. Chem.*, **152**. 405, 1926; K. C. Sen and N. R. Dhar, *Koll. Zeit.*, **34**. 270, 1924; S. S. Bhatnagar and J. L. Sehgal, *ib.*, **39**. 264, 1926; A. Janek, *ib.*, **32**. 252, 1923; M. Copisarow, *ib.*, **47**. 60, 1929; M. L. Dundon, *Journ. Amer. Chem. Soc.*, **45**. 2658, 1923; E. C. H. Davies, *ib.*, **44**. 2698, 1922; A. Steopoe, *Bul. Soc. Romana Stiinte*, **27**. 51, 1924; H. McGuigan, *Science*, (2), **54**. 78, 1921; F. G. Toyhorn and S. C. Blacktin, *Trans. Faraday Soc.*, **19**. 433, 1923; W. R. Hodgkinson and J. Young, *B.A. Rep.*, 676, 1892; C. K. Jablczynsky and S. Kobryner, *Bull. Soc. Chim.*, (4), **39**. 383, 1926; C. K. Jablczynsky, *ib.*, (4), **33**. 1592, 1923; *Koll. Zeit.*, **40**. 22, 1926; *Rocz. Chem.*, **3**. 228, 1923; **7**. 150, 1927; C. K. Jablczynsky and A. Klein, *ib.*, **3**. 479, 1923; R. Fricke, *Zeit. phys. Chem.*, **107**. 41, 1923; R. Hunt, *Mem. Chem. Soc.*, **2**. 316, 1845; G. Linck, *Chem. Erde*, **4**. 88, 1928; F. Pannach, *ib.*, **4**. 598, 1930; H. Westerhoff, *Untersuchungen an einem System Liesegangscher periodischer Fällungen*, Münster, 1929; H. W. Morse, *Journ. Phys. Chem.*, **34**. 1554, 1930; W. W. Siebert, *Biochem. Zeit.*, **220**. 487, 1930; F. M. Shemyalein, *Koll. Zeit.*, **50**. 58, 1930; D. N. Ghosh, *Journ. Indian Chem. Soc.*, **7**. 509, 1930.

[10] N. A. Orloff, *Chem. Ztg.*, **31**. 1182, 1907.

[11] T. Thomson, *Ann. Phil.*, **16**. 321, 1820; H. Moser, *Chemische Abhandlung über das Chrom*, Wien. 1824; *Schweigger's Journ.*, **42**. 99, 1824; J. F. Bahr, *Oefvers. Akad. Förh. Stockholm*, **9**. 160, 1852; K. Herrmann, M. Hosenfeld and N. Schönfeldt, *Wiss. Veroff. Siemens-Konz.*, **5**. 189, 1926; F. Mylius and J. von Wrochem, *Wiss. Phys. Tech. Reichsanst.*, **3**. 459, 1900; *Ber.*, **33**. 3692, 1900; F. T. Frerichs, *ib.*, **7**. 800, 1874; *Gött. Nachr.*, 349, 1874; M. Copisarow, *Koll. Zeit.*, **47**. 60, 1928; E. Carrière and P. Castel, *Compt. Rend.*, **187**. 1292, 1928; J. Precht, *Ann. Physik*, (4), **1**. 421, 1900; F. Kuhlmann, *Liebig's Ann.*, **41**. 229, 1842; J. Morris, *ib.*, **213**. 257, 1882; H. von Foullon, *Jahresb. geol. Reichsanst. Wien*, **40**. 421, 1890; H. Kämmerer, *Zeit. anal. Chem.*, **12**. 375, 1873; G. N. Wyrouboff, *Bull. Soc. Min.*, **14**. 203, 235, 327, 1892; **32**. 6, 1909; A. de Schulten, *ib.*, **27**. 129, 1905; L. Bourgeois, *ib.*, **2**. 123, 1879; *Chem. News*, **39**. 123, 1879; *Compt. Rend.*, **88**. 382, 1879; M. Barre, *ib.*, **158**. 495, 1914; P. Bary, *ib.*, **130**. 776, 1900; A. Rakowsky, *Bull. Acad. St. Petersburg*, (6), **2**. 905, 1908; M. Siewert, *Zeit. ges. Naturw.*, **19**. 29, 1862; A. Fock, *Zeit. Kryst.*, **32**. 250, 1900; J. Milbauer, *Chem. Ztg.*, **40**. 587, 1916; H. G. F. Schröder, *Dichtigkeitsmessungen*, Heidelberg, 1873; *Liebig's Ann.*, **172**. 298, 1874; **173**. 72, 1874; **174**. 249, 1874; H. Schwarz, *Dingler's Journ.*, **198**. 159, 1870; F. Mohr, *ib.*, **21**. 266, 1874; F. Kohlrausch, *Sitzber. Akad. Berlin*, 90, 1897; 1218, 1904; *Zeit. phys. Chem.*, **44**. 233, 1903; **64**. 129, 1908; F. Kohlrausch and F. Rose, *ib.*, **12**. 241, 1893; F. Guthrie, *Journ. Chem. Soc.*, **47**. 94, 1885; J. B. Hannay, *Chem. News*, **34**. 256, 1877; H. Caron and D. A. Raquet, *Bull. Soc. Chim.*, (3), **35**. 1064, 1906; A. Duncan, *Proc. Phil. Soc. Glasgow*, **3**. 7, 1853; *Phil. Mag.*, (3), **36**. 109, 1850; J. D. Smith, *ib.*, (3), **8**. 260, 1836; E. Schweizer, *Journ. prakt. Chem.*, (1), **39**. 261, 1846; M. Gröger, *Zeit. anorg. Chem.*, **54**. 187, 1907; **58**. 414, 1908; F. Stolba, *Sitzber. Böhm. Akad.*, 327, 1873; *Chem. Centr.*, (3), **5**. 122, 1874; H. H. Hosford and H. C. Jones, *Amer. Chem. Journ.*, **46**. 240, 1911; S. F. Howard and H. C. Jones, *ib.*, **48**. 580, 1913; M. R. Nayar, H. E. Watson and J. J. Sudborough, *Journ. Indian Inst. Science*, **7**. 53, 1924; K. S. Nargund and H. E. Watson, *ib.*, **9**. 149, 1926; M. R. Nayar and H. E. Watson, *Proc. Asiatic Soc. Bengal*, **18**. 73, 1922; J. W. Döbereiner, *Schweigger's Journ.*, **22**. 476, 1818: *Trommsdorff's Journ.*, **5**. 250, 1818; A. Schafarik, *Sitzber. Akad. Wien*, **47**. 256, 1863; *Journ. prakt. Chem.*, (1), **90**. 1, 1863; H. Rose, *Pogg. Ann.*, **95**. 426, 1855; E. Dumesnil, *Ann. Chim. Phys.*, (7), **20**. 125, 1900; F. J. Malaguti, *ib.*, (3), **51**. 346, 1857; P. D. Chrustschoff and A. Martinoff, *ib.*, (6), **11**. 234, 1887; B. Guerini, *Volumétrie physico-chimique de précision avec les conductivités comme indicateurs*, Lausanne, 1922; I. Meschtschersky, *Zeit. anal. Chem.*, **21**. 399, 1882; C. R. Fresenius, *ib.*, **29**. 418, 1890; **30**. 672, 1891; W. Autenrieth, *Ber.*, **37**. 3882, 1904; K. Preis and B. Rayman, *ib.*, **13**. 342, 1880; A. Naumann, *ib.*, **37**. 4329, 1904; **42**. 3790, 1909; D. Vorländer and H. Hempel, *ib.*, **60**. B, 845, 1927; M. A. Iljinsky, A. A. Balandin, M. V. Gaurdovskaja and B. T. Poliak, *Journ. Russ. Phys. Chem. Soc.*, **58**. 241, 1926; C. Reichard, *Chem. Ztg.*, **27**. 877, 1903; G. Zerr and G. Rubencamp, *Handbuch der Farbenfabrikation*, Berlin, 345, 1909; London, 126, 1908; F. Ransom, *Pharm. Journ.*, (3), **13**. 626, 1883; C. H. D. Bödecker, *Die Beziehungen*

zwischen Dichte und Zusammensetzung bei festen und liquiden Stoffen, Leipzig, 1860 ; M. Scholtz and R. Abegg, *Zeit. Elektrochem.*, **12**. 425, 1906 ; A. Pool, *Pharm. Weekbl.*, **40**. 605, 1903 ; E. Herlinger, *Zeit. Kryst.*, **62**. 454, 1925 ; L. Kahlenberg and W. J. Trautmann, *Trans. Amer. Electrochem. Soc.*, **39**. 377, 1921 ; E. Fleischer, *Journ. prakt. Chem.*, (2), **5**. 326, 1872 ; L. Schulerud, *ib.*, (2), **19**. 36, 1879 ; H. Baubigny, *Bull. Soc., Chim.*, (4), **1**. 58, 1907 ; L. H. Duschak, *Journ. Amer. Chem. Soc.*, **30**. 1827, 1908 ; L. M. Henderson and F. C. Kracek, *ib.*, **49**. 738, 1927 ; N. W. Fischer, *Kastner's Arch.*, **9**. 356, 1826 ; H. Golblum, *Journ. Chim. Phys.*, **7**. 289, 1909 ; J. A. Atanasiu, *ib.*, **23**. 501, 1926 ; J. F. G. Hicks and W. A. Craig, *Journ. Phys. Chem.*, **26**. 563, 1922 ; F. Rinne, *Centr. Min.*, 161, 1904 ; K. W. Flöroff, *Zeit. Koll.*, **36**. 215, 1925 ; W. R. Hodgkinson and J. Young, *B.A. Rep.*, 676, 1892 ; O. Ruff and E. Ascher, *Zeit. anorg. Chem.*, **185**. 369, 1930 ; O. Ruff, *ib.*, **185**. 387, 1930 ; A. Osann, *Zeit. Kryst.*, **23**. 588, 1894 ; A. Dietze, *ib.*, **19**. 447, 1891 ; B. Gossner and F. Mussgnug, *ib.*, **75**. 410, 1930 ; B. Gossner, *Centr. Min.*, 101, 1925.

[12] L. M. Henderson and F. C. Kracek, *Journ. Amer. Chem. Soc.*, **49**. 738, 1927.

[13] A. Atterberg, *Svenska Akad. Handl.*, **12**. 5, 1873 ; J. C. G. de Marignac, *Arch. Sciences Genève*, (2), **44**. 204, 1872 ; H. C. Creuzberg, *Dingler's Journ.*, **161**. 449, 1862 ; B. Glassmann, *Ber.*, **40**. 2602, 1907 ; N. A. Orloff, *Zeit. anorg. Chem.*, **79**. 365, 1913 ; B. Bleyer and A. Moormann, *ib.*, **76**. 70, 1912.

[14] M. R. Nayer, H. E. Watson and J. J. Sudborough, *Journ. Indian Inst. Science*, **7**. 53, 1924 ; G. N. Wyrouboff, *Bull. Soc. Min.*, **12**. 69, 1890 ; **14**. 253, 1891 ; L. N. Vauquelin, *Ann. Chim. Phys.*, (1), **70**. 70, 1809 ; F. J. Malaguti and M. Sarzeau, *ib.*, (3), **9**. 431, 1843 ; H. Topsöe and C. Christiansen, *ib.*, (5), **1**. 5, 1874 ; *Danske Selsks. Förh.*, (5), **9**. 57, 1873 ; F. Rüdorff, *Ber.*, **21**. 3047, 1888 ; F. Mylius and R. Funk, *ib.*, **30**. 1718, 1897 ; A. Naumann, *ib.*, **37**. 4328, 1904 ; M. Wein, *Ann. Physik*, (5), **1**. 400, 1929 ; A. Murmann, *Sitzber. Akad. Wien*, **27**. 175, 1857 ; W. J. Grailich, *ib.*, **27**. 175, 1857 ; W. J. Grailich and V. von Lang, *ib.*, **27**. 21, 1857 ; C. von Hauer, *ib.*, **39**. 441, 1860 ; W. Kohlrausch, *Sitzber. Akad. Berlin*, 90, 1897 ; K. F. Slotte, *Wied. Ann.*, **14**. 19, 1881 ; J. Milbauer, *Chem. Ztg.*, **40**. 587, 1916 ; P. Walden, *Zeit. phys. Chem.*, **1**. 536, 1887 ; L. Longchambon, *Bull. Soc. Min.*, **45**. 161, 1922 ; C. Gaudefroy, *ib.*, **42**. 332, 1919 ; F. W. Clarke, *Amer. Journ. Science*, (3), **14**. 281, 1877 ; H. G. K. Westenbrink, *Proc. Akad. Amsterdam*, **29**. 1223, 1926 ; M. W. Porter, *Proc. Roy. Soc.*, **109**. A, 78, 1925 ; *Zeit. Kryst.*, **63**. 557, 1926 ; A. Fock, *ib.*, **4**. 583, 1880 ; A. E. H. Tutton and M. W. Porter, *ib.*, **51**. 53, 1912 ; *Min. Mag.*, **16**. 169, 1912 ; H. Dufet, *Compt. Rend.*, **99**. 992, 1884 ; G. Viard, *ib.*, **112**. 1004, 1891 ; *Bull. Soc. Chim.*, (3), **5**. 934, 1891 ; A. Heydweiller, *Ann. Physik*, (4), **37**. 739, 1912 ; H. Clausen, *Weitere Beiträge zur Beziehung zwischen Dichte und Dissociationsgrad wässeriger Salzlosungen*, Bostock, 1911 ; T. V. Barker, *Journ. Chem. Soc.*, **99**. 1328, 1911 ; S. H. C. Briggs, *ib.*, **85**. 672, 677, 1904 ; H. G. F. Schröder, *Dichtigkeitsmessungen*, Heidelberg, 1873 ; *Liebig's Ann.*, **174**. 249, 1874 ; M. Gröger, *Zeit. anorg. Chem.*, **54**. 188, 1907 ; **58**. 412, 1908 ; E. Dittler, *ib.*, **168**. 309, 1928 ; A. Stanley, *Chem. News*, **54**. 194, 1886 ; H. Kopp, *Liebig's Ann.*, **42**. 97, 1842 ; C. H. D. Bödeker, *Die Beziehungen zwischen Dichte und Zusammensetzung bei festen und liquiden Stoffen*, Leipzig, 1860 ; T. Thomson, *Phil. Trans.*, **117**. 224, 1827 ; E. F. Anthon, *Repert. Pharm.*, **34**. 248, 1830 ; E. Schweizer, *Journ. prakt. Chem.*, (1), **39**. 261, 1846 ; F. A. Henglein, *Zeit. anorg. Chem.*, **120**. 77, 1912 ; A. Duffour, *Bull. Soc. Min.*, **42**. 242, 247, 1919 ; *Compt. Rend.*, **169**. 73, 1919 ; C. Schaefer and M. Schubert, *Zeit. physik*, **7**. 297, 1921 ; S. Rösch and M. Stürenburg, *Zeit. Kryst.*, **65**. 588, 1927 ; G. Canneri, *Gazz. Chim. Ital.*, **55**. 611, 1925.

[15] J. Prüssen and H. Philippona, *Liebig's Ann.*, **149**. 92, 1869 ; L. Bieler, *ib.*, **151**. 223, 1869 ; F. J. Malaguti and M. Sarzeau, *Ann. Chim. Phys.*, (3), **9**. 431, 1844 ; A. Bensch, *Pogg. Ann.*, **55**. 97, 1842 ; T. Thomson, *Phil. Mag.*, **3**. 81, 1828 ; J. J. Berzelius, *Schweigger's Journ.*, **22**. 53, 1818 ; *Ann. Chim. Phys.*, (2), **17**. 7, 1821 ; *Pogg. Ann.*, **1**. 34, 1824 ; J. Schulze, *Zeit. anorg. Chem.*, **10**. 148, 1895 ; G. Krüss and O. Unger, *ib.*, **8**. 45, 1895 ; S. H. C. Briggs, *ib.*, **56**. 254, 1908 ; *Journ. Chem. Soc.*, **83**. 394, 1903 ; **85**. 672, 677, 1904 ; 242, 1929 ; M. Gröger, *Monatsh.*, **25**. 520, 1904 ; *Anz. Akad. Wien*, **17**. 62, 1880 ; *Sitzber. Akad. Wien*, **113**. 156, 1904 ; *Zeit. anorg. Chem.*, **54**. 185, 1907 ; **58**. 412, 1908 ; **66**. 8, 1910 ; **70**. 135, 1911 ; C. O. Weber, *Dingler's Journ.*, **279**. 139, 210, 232, 284, 1891 ; J. Milbauer, *Chem. Ztg.*, **40**. 587, 1916 ; C. Freese, *Ber.*, **2**. 478, 1868 ; A. Naumann, *ib.*, **137**. 4329, 1904 ; H. Kopp, *Liebig's Ann.*, **57**. 386, 1846 ; M. Prud'homme and F. Binder, *Bull. Soc. Chim.*, (2), **37**. 194, 1883 ; M. L. Boyan, *Trans. Amer. Cer. Soc.*, **10**. 124, 1908 ; L. Bock, *Zeit. Koll.*, **20**. 145, 1917 ; E. C. Franklin, *Amer. Chem. Journ.*, **20**. 830, 1898 ; F. Rose, *Die Mineralfarben*, Leipzig, 270, 1916 ; J. G. Gentele, *Lehrbuch der Farbenfabrikation*, Braunschweig, **2**. 205, 1909 ; G. Zerr and G. Rübencamp, *Handbuch der Farbenfabrikation*, Berlin, 345, 1909 ; London, 126, 1908 ; S. Tschelnitz, *Farbenchemie*, Wien, 56, 1857 ; W. A. Lampadius, *Journ. tech. oekon. Chem.*, **4**. 444, 1829 ; **16**. 350, 1833 ; W. Ackroyd, *Chem. News*, **67**. 27, 64, 1893 ; G. Viard, *Compt. Rend.*, **112**. 1004, 1891 ; *Bull. Soc. Chim.*, (3), **5**. 934, 1891 ; K. Preis and B. Raymann, *Sitzber. Böhm. Ges.*, 507, 1879 ; B. Skormin, *Ueber das basische Chromate bzw. auch die chromsauren Kaliumdoppelsalze des Zink, Cadmium, Kupfer- und Quecksilberoxyds*, Berlin, 1896 ; L. Vanino and F. Ziegler, *Chem. Ztg.*, **49**. 266, 1925 ; *Chem. Trade Journ.*, **76**. 456, 1925 ; H. S. Taylor and G. I. Lavin, *Journ. Amer. Chem. Soc.*, **52**. 1910, 1930.

[16] L. Schulerud, *Journ. prakt. Chem.*, (2), **19**. 38, 1879 ; P. and M. M. Richter, *Ber.*, **15**. 1489, 1882 ; E. Jäger and G. Krüss, *ib.*, **22**. 2049, 1899 ; L. N. Vauquelin, *Ann. Chim. Phys.*, (1), **70**. 70, 1809 ; N. A. E. Millon, *ib.*, (3), **18**. 365, 1846 ; C. Freese, *Pogg. Ann.*, **40**. 81, 1870 ; H. Rose, *ib.*, **53**. 124, 1841 ; C. M. Marx, *Schweigger's Journ.*, **66**. 107, 1832 ; S. Darby, *Journ. Chem. Soc.*, **1**. 24, 1849 ; *Liebig's Ann.*, **65**. 204, 1843 ; A. Geuther, *ib.*, **106**. 247, 1858 ; M. Gröger,

Zeit. anorg. Chem., **54**. 191, 1907 ; **58**. 419, 1908 ; S. Löwenthal, *Zur Kenntniss der chlor- und amidochromsauren Salze*, Bostock, 1893 ; *Zeit. anorg. Chem.*, **6**. 367, 1894 ; F. Fichter and G. Oesterheld, *ib.*, **76**. 350, 1912 ; A. J. Cox, *ib.*, **40**. 155, 1904 ; **50**. 242, 1906 ; *Ueber basische Quecksilbersalze*, Leipzig, 1904 ; *Journ. Amer. Chem. Soc.*, **28**. 1694, 1906 ; O. D. Swett, *ib.*, **31**. 928, 1908 ; E. C. Franklin, *Amer. Chem. Journ.*, **29**. 63, 1907 ; F. W. Clarke and D. Stern, *ib.*, **3**. 353, 1881 ; B. Skormin, *Ueber das basische Chromate bzw. auch die chromsauren Kaliumdoppelsalze des Zink-, Cadmium, Kupfer- und Quecksilberoxyds*, Berlin, 1896 ; C. Hensgen, *Rec. Trav. Chim. Pays-Bas*, **5**. 195, 1886 ; F. M. Litterscheid, *Arch. Pharm.*, **241**. 308, 1903 ; A. Gawalowsky, *Pharm. Post*, **39**. 602, 1906 ; J. L. Gay Lussac and L. J. Thénard, *Recherches physicochimiques*, Paris, **1**. 313, 1811 ; C. H. Hirzel, *Ueber die Einwirkungen des Quecksilbers auf des Ammoniak und die Ammoniaksalze*, Leipzig, 1852 ; *Liebig's Ann.*, **84**. 258, 1852 ; *Zeit. Pharm.*, **2**. 6, 1870 ; L. Gmelin, *Handbook of Chemistry*, London, **6**. 113, 1851 ; A. A. Hayes, *Amer. Journ. Science*, (2), **20**. 409, 1855 ; S. M. Godon de St. Menin, *Ann. Chim. Phys.*, (1), **53**. 222, 1805 ; *Ann. Musée Hist. Nat.*, **4**. 238, 1804 ; *Phil. Mag.*, **20**. 266, 1805 ; *Gehlen's Journ.*, **5**. 598, 1805 ; R. Behrend, *Zeit. phys. Chem.*, **11**. 480, 1893 ; R. H. Brett, *Phil. Mag.*, (3), **10**. 95, 1837 ; A. Caillot, *Ann. Chim. Phys.*, (2), **42**. 263, 1829 ; F. Rose, *Die Mineralfarben*, Leipzig, 270, 1916 ; A. Naumann, *Ber.*, **37**. 4329, 1904 ; **43**. 314, 1910 ; J. A. Atanasiu, *Journ. Chim. Phys.*, **23**. 501, 1926.

[17] A. J. Fairrie, *Journ. Chem. Soc.*, **4**. 300, 1851 ; A. Maus, *Pogg. Ann.*, **11**. 82, 1827 ; L. Petrik, *Tonind. Ztg.*, **15**. 101, 1891 ; C. W. Eliot and F. H. Storer, *Proc. Amer. Acad.*, **5**. 207, 1862 ; *Chem. News*, **6**. 121, 136, 145, 157, 169, 182, 207, 217, 1862 ; E. Fleischer, *Arch. Pharm.*, (3), **3**. 300, 1873 ; M. Gröger, *Ber.*, **35**. 3420, 1902 ; M. Siewert, *Zeit. ges. Naturwiss.*, **19**. 33, 1862 ; N. A. Orloff, *Zeit. anorg. Chem.*, **79**. 365, 1913 ; L. Blanc, *Ann. Chim. Phys.*, (10), **6**. 182, 1926 ; *Étude de quelques transformations observées au cours de la calcination des sesquioxydes de fer, de chrome, et d'aluminium*, Paris, 1926 ; S. H. C. Briggs, *Journ. Chem. Soc.*, 242, 1929.

[18] R. E. Meyer, *Liebig's Ann.*, **150**. 137, 1869 ; C. Winkler, *Journ. prakt. Chem.*, (1), **94**. 1, 1865 ; (1), **95**. 414, 1865 ; (1), **98**. 344, 1866 ; (1), **102**. 273, 1867.

[19] W. Crookes, *Chem. News*, **8**. 255, 1863 ; E. Carstanjen, *Journ. prakt. Chem.*, (2), **2**. 56, 1870 ; M. Lachaud and C. Lepierre, *Compt. Rend.*, **113**. 196, 1891 ; M. Gröger, *Zeit. anorg. Chem.*, **109**. 226, 1919 ; E. Rupp and M. Zimmer, *Zeit. anorg. Chem.*, **33**. 156, 1903 ; P. E. Browning and G. P. Hutchins, *ib.*, **22**. 380, 1900 ; *Amer. Journ. Science*, (4), **8**. 460, 1889 ; L. F. Hawley, *Journ. Amer. Chem. Soc.*, **29**. 301, 1917 ; E. Willm, *Ann. Chim. Phys.*, (4), **5**. 59, 1865 ; *Bull. Soc. Chim.*, (2), **2**. 89, 1864 ; J. W. Retgers, *Zeit. phys. Chem.*, **8**. 39, 1891 ; M. Hebberling, *Liebig's Ann.*, **134**. 11, 1865 ; W. Strecker, *ib.*, **135**. 207, 1865 ; G. Canneri, *Gazz. Chim. Ital.*, **52**. i, 33, 1922.

[20] A. Beringer, *Liebig's Ann.*, **42**. 143, 1842 ; J. F. John, *Schweigger's Journ.*, **3**. 378, 1811 ; S. Jolin, *Bull. Soc. Chim.*, (2), **21**. 533, 1874 ; P. T. Cleve, *ib.*, (2), **29**. 497, 1874 ; *Bihang. Svenska Akad. Hand.*, 2, 1874 ; *Chem. News*, **53**. 100, 1886 ; M. M. Pattison and J. Clarke, *ib.*, **16**. 259, 1867 ; A. Loose, *Studien über die seltenen Erden aus der Cer- und Ytter-gruppe*, München, 1892 ; G. Krüss and A. Loose, *Zeit. anorg. Chem.*, **3**. 103, 1893 ; C. R. Böhm, *Die Zerlegbarkeit des Praseodyms und Darstellung seltener Erden mit Hilfe neuen Trennungsmethode*, Halle a. S., 1900 ; *Zeit. angew. Chem.*, **15**. 372, 1282, 1902 ; *Pharm. Ztg.*, **47**. 297, 1902 ; W. Muthmann and C. R. Böhm, *Ber.*, **33**. 42, 1900 ; N. J. Berlin, *Svenska Akad. Handl.*, 212, 1835 ; A. Brauell, *Beiträge zur Kenntnis des Cerium*, Jena, 1875 ; L. M. Dennis and B. Dales, *Journ. Amer. Chem. Soc.*, **24**. 400, 1902 ; J. E. Egan and C. W. Balke, *ib.*, **35**. 365, 1913 ; B. S. Hopkins and C. W. Balke, *ib.*, **38**. 2332, 1916 ; C. James, *ib.*, **34**. 757, 1912 ; F. Frerichs and F. Smith, *Liebig's Ann.*, **191**. 365, 1878 ; O. Popp, *ib.*, **131**. 197, 1864 ; G. Jantsch and A. Ohl, *Ber.*, **44**. 1274, 1911 ; N. A. Orloff, *Chem. Ztg.*, **31**. 562, 1907 ; P. B. Sardar, *Bull. Soc. Chim.*, (4), **39**. 1390, 1926 ; *Ann. Chim. Phys.*, (10), **8**. 207, 1927 ; L. Haber, *Monatsh.*, **18**. 667, 1897 ; F. Zambonini and G. Carobbi, *Rend. Accad. Napoli*, (3), **31**. 17, 1925 ; G. Carobbi, *Gazz. Chim. Ital.*, **56**. 76, 1926 ; *Atti Accad. Lincei*, (5), **33**. ii, 416, 1924 ; H. T. S. Britton, *Journ. Chem. Soc.*, **125**. 1875, 1924 ; E. Baur, *German Pat., D.R.P.* 120013, 1900 ; H. C. Holden and C. James, *Journ. Amer. Chem. Soc.*, **36**. 638, 1914 ; R. J. Meyer and J. Wuorinen, *Zeit. anorg. Chem.*, **80**. 7, 1913 ; H. Moissan and A. Étard, *Compt. Rend.*, **122**. 573, 1896.

[21] S. M. Godon de St. Menin, *Ann. Chim. Phys.*, (1), **53**. 222, 1805 ; *Ann. Musée Hist. Nat.*, **4**. 238, 1804 ; *Phil. Mag.*, **20**. 266, 1805 ; G. A. Quesneville, *Journ. Pharm. Chim.*, (1), **16**. 131, 1830 ; M. Blondel, *Bull. Soc. Chim.*, (3), **19**. 218, 1898 ; M. Weibull, *Acta Lund Univ.*, (2), **18**. 57, 1882 ; L. Haber, *Monatsh.*, **18**. 667, 1897 ; P. Krishnamurti and B. B. Dey, *Zeit. anorg. Chem.*, **158**. 94, 1926 ; F. P. Venable and L. V. Giles, *Journ. Amer. Chem. Soc.*, **40**. 1653, 1918 ; S. H. C. Briggs, *Journ. Chem. Soc.*, 242, 1929.

[22] C. Palmer, *Amer. Chem. Journ.*, **17**. 374, 1895 ; W. Muthmann and E. Bauer, *Ber.*, **33**. 2028, 1900 ; E. Baur, *German Pat., D.R.P.* 120012, 1900 ; L. Haber, *Monatsh.*, **18**. 687, 1897 ; *Sitzber. Akad. Wien*, **106**. 690, 1897 ; J. Chydenius, *Pogg. Ann.*, **119**. 53, 1863 ; J. J. Berzelius, *ib.*, **16**. 412, 1829 ; H. T. S. Britton, *Journ. Chem. Soc.*, **123**. 1429, 1923.

[23] J. J. Berzelius, *Schweigger's Journ.*, **22**. 53, 1818 ; *Pogg. Ann.*, **1**. 34, 1824 ; *Ann. Chim. Phys.*, (2), **17**. 1, 1821 ; F. J. Malaguti, *ib.*, (2), **61**. 433, 1836 ; P. Grouvelle, *ib.*, (1), **17**. 349, 1821 ; T. Leykauf, *Journ. prakt. Chem.*, (1), **19**. 127, 1840 ; (2), **19**. 127, 1892 ; C. Lauth and G. Dutailly, *Monit. Scient.*, (4), **2**. 1037, 1888 ; G. Steinbrecht, *Sprech.*, **34**. 123, 1891 ; H. Stein, *ib.*, **20**. 825, 1888 ; L. Petrik, *Tonind. Ztg.*, **15**. 101, 1891 ; A. S. Watts, *Trans. Amer. Cer. Soc.*, **13**. 301, 1911 ; F. Rhead, *ib.*, **13**. 324, 1911 ; R. C. Purdy and G. H. Brown, *ib.*, **11**. 228, 1909 : R. C. Purdy and A. S. Rea, *ib.*, **12**. 518, 1911 ; R. C. Purdy, *ib.*, **5**. 249, 1903 ; **14**. 178, 1912 ;

W. A. Hall, *ib.*, **4**. 230, 1902 ; H. A. Seger, *Gesammelte Schriften*, Berlin, 541, 1908 ; Easton, Pa., **2**. 663, 1902 ; W. A. Lethbridge, *Trans. Cer. Soc.*, **3**. 9, 1903.

[24] J. G. Lehmann, *Nov. Comm. Acad. Petrop.*, **12**. 356, 1766 ; *De nova mineræ plumbi specie crystallina pubra*, Petropoli, 1766 ; P. S. Pallas, *Reise durch verschiedene Provinzen des Russischen Reichs*, St. Petersburg, **2**. 235, 1771 ; L. C. H. Macquart, *Journ. Phys.*, **34**. 389, 1789 ; J. G. Wallerius, *Systema mineralogicum*, Wien, 1778 ; A. G. Werner, *Von den äusserlichen Kennzeichen der Fossilien*, Leipzig, 296, 1774 ; L. N. Vauquelin, *ib.*, **45**. 393, 1794 ; **46**. 152, 311, 1798 ; *Journ. Mines.*, **6**. 737, 1797 ; *Nicholson's Journ.*, **2**. 387, 441, 1799 ; *Phil. Mag.*, **1**. 279, 361, 1798 ; **2**. 74, 1798 ; *Ann. Chim. Phys.*, (1), **25**. 21, 194, 1798 ; (1), **70**. 70, 1809 ; R. J. Haüy, *Traité de minéralogie*, Paris, **3**. 3467, 1801 ; F. S. Beudant, *Traité élémentaire de minéralogie*, Paris, **2**. 669, 1832 ; A. Breithaupt, *Vollständiges Handbuch der Mineralogie*, Dresden, **2**. 262, 1841 ; W. H. Miller, *Introduction to Mineralogy*, London, 557, 1852 ; F. von Kobell, *Grundzüge der Mineralcgie*, Nürnberg, 282, 1838 ; J. F. L. Hausmann, *Handbuch der Mineralogie*, Göttingen, 1086, 1813.

[25] C. H. Pfaff, *Schweigger's Journ.*, **18**. 72, 1816 ; J. J. Berzelius, *ib.*, **22**. 54, 1818 ; R. Hermann, *Pogg. Ann.*, **28**. 162, 1833 ; C. F. Schönbein, *ib.*, **15**. 263, 1838 ; C. Bärwald, *Zeit. Kryst.*, **7**. 170, 1883 ; P. Groth, *ib.*, **7**. 592, 1883 ; P. Niggli, *ib.*, **56**. 42, 1922 ; F. Brandenburg, *Scherer's Ann.*, **3**. 61, 1820 ; *Ann. Gén. Science Phys.*, **1**. 85, 1819 ; A. Liversidge, *Proc. Roy. Soc. New South Wales*, **28**. 316, 1894 ; *Chem. News*, **74**. 113, 1896 ; H. Golblum and G. Stoffella, *Journ. Chim. Phys.*, **8**. 141, 1910 ; M. Gröger, *Zeit. anorg. Chem.*, **54**. 192, 1907 ; **58**. 424, 1908 ; **108**. 270, 1919 ; **109**. 220, 1920 ; A. J. Cox, *ib.*, **50**. 234, 1906 ; *Ueber basische Quecksilbersalze*, Leipzig, 1904 ; *Journ. Amer. Chem. Soc.*, **28**. 1694, 1906 ; W. E. Garrigues, *ib.*, **20**. 508, 1898 ; N. S. Manross, *Liebig's Ann.*, **82**. 348, 1852 ; A. Drevermann, *ib.*, **87**. 121, 1853 ; **89**. 38, 1854 ; H. Vohl, *ib.*, **88**. 114, 1853 ; **106**. 127, 1858 ; L. Bourgeois, *Bull. Soc. Min.*, **10**. 188, 1887 ; *Bull. Soc. Chim.*, (2), **47**. 544, 883, 1887 ; *Compt. Rend.*, **104**. 130, 1887 ; A. C. Becquerel, *ib.*, **63**. 6, 1866 ; **76**. 245, 1873 ; **79**. 82, 1874 ; P. Schützenberger, *ib.*, **98**. 1522, 1884 ; C. Marie, *ib.*, **130**. 1032, 1900 ; L. Godard, *ib.*, **106**. 547, 1888 ; G. Chancel, *ib.*, **43**. 927, 1856 ; S. Meunier, *ib.*, **87**. 656, 1874 ; L. Vignon, *Bull. Soc. Chim.*, (4), **5**. 675, 1909 ; *Compt. Rend.*, **148**. 1195, 1329, 1909 ; M. Barre, *ib.*, **158**. 497, 1914 ; C. Lüdeking, *ib.*, **114**. 544, 1892 ; A. de Schulten, *ib.*, **136**. 1444, 1903 ; *Bull. Soc. Min.*, **27**. 130, 1904 ; M. Lachaud and C. Lepierre, *Compt. Rend.*, **110**. 1135, 1890 ; *Bull. Soc. Chim.*, (3), **6**. 230, 1891 ; J. B. Senderens, *ib.*, (3), **6**. 805, 1891 ; M. Fraudel, *Dingler's Journ.*, **214**. 499, 1874 ; J. Fanzoy, *Stamm's Illustr. Wochenschr.*, 156, 1863 ; *Dingler's Journ.*, **169**. 156, 1863 ; A. Habich, *ib.*, **140**. 126, 1856 ; A. Prinvault, *ib.*, **220**. 259, 1875 ; H. Schwarz, *ib.*, **186**. 31, 1867 ; M. Riot and B. Declisse, *Génie Ind.*, 196, 1853 ; *Dingler's Journ.*, **128**. 195, 1853 ; C. O. Weber, *ib.*, **279**. 139, 210, 232, 284, 1891 ; *Journ. Soc. Chem. Ind.*, **4**. 671, 1885 ; **10**. 709, 1891 ; A. Winterfeld, *Dingler's Journ.*, **86**. 438, 1848 ; *Polyt. Arch.*, 47, 1842 ; F. Kuhlmann, *Liebig's Ann.*, **41**. 228, 1842 ; H. Kopp, *Liebig's Ann. Suppl.*, **3**. 107, 296, 1865 ; W. E. Fuss, *Journ. prakt. Chem.*, (1), **18**. 230, 1833 ; R. F. Marchand, *ib.*, (2), **19**. 65, 1840 ; M. Rosenfeld, *ib.*, (2), **15**. 240, 1877 ; L. Schulerud, *ib.*, (2), **19**. 36, 1879 ; J. Rosenthal, *Ueber die elektrische Leitfähigkeit fester Elektrolyte bei verschiedenen Temperaturen*, Erlangen, 1891 ; *Wied. Ann.*, **43**. 708, 1891 ; E. Lay, *Ueber Silicium-Stickstoff-Wasserstoff Verbindungen*, München, 58, 1910 ; W. Lenze, *Zur Kenntnis kolloidaler Metalle und ihrer Verbindungen*, Erlangen, 30, 1904 ; W. E. Dawson, *Min. Mag.* (*Minutes*), **6**. 18, 1885 ; H. C. Sorby, *ib.*, **2**. 1, 1878 ; G. N. Ridley, *Chem. News*, **125**. 12, 1922 ; F. Hessenberg, *Mineralogische Notizen*, Frankfurt, **3**. 27, 1860 ; *Abhand Nat. Ges. Senckenberg*, **3**. 281, 1861 ; H. Dauber, *Sitzber. Akad. Wien.*, **32**. 19, 1858 ; *Pogg. Ann.*, **106**. 150, 1859 ; F. Wöhler and J. von Liebig, *ib.*, **21**. 580, 1830 ; J. von Liebig, *Mag. Pharm.*, **35**. 358, 1831 ; H. C. Germs, *De thermische Analyse van Loodsulfaat, -Chromaat, -Molybdaat en -Wolframaat en van hun binaire Combinaties*, Gröningen, 1917 ; F. M. Jäger and H. C. Germs, *Zeit. anorg. Chem.*, **119**. 154, 1921 ; D. Strömholm, *ib.*, **38**. 443, 1904 ; R. Weinland and F. Paul, *ib.*, **129**. 257, 1923 ; G. Tammann and Q. A. Mansuri, *ib.*, **126**. 127, 1923 ; W. Grahmann, *ib.*, **81**. 306, 1913 ; K. Jellinek and H. Ens, *ib.*, **124**. 196, 1922 ; F. Paneth, *Zeit. Elektrochem.*, **28**. 113, 1922 ; G. von Hevesy and F. Paneth, *Zeit. anorg. Chem.*, **82**. 323, 1913 ; G. von Hevesy and E. Rona, *Zeit. phys. Chem.*, **89**. 304, 1915 ; F. Kohlrausch, *ib.*, **44**. 197, 1903 ; **64**. 159, 1908 ; F. Kohlrausch and F. Rose, *ib.*, **12**. 241, 1893 ; R. Labes, *ib.*, **116**. 1, 1925 ; R. Lorenz and W. Herz, *ib.*, **135**. 374, 1924 ; F. Auerbach and H. Pick, *Arb. Ges. Amt.*, **45**. 167, 1913 ; K. Beck and P. Stegmüller, *ib.*, **34**. 449, 1910 ; *Zeit. Elektrochem.*, **17**. 846, 1911 ; K. Elbs and R. Nübling, *ib.*, **9**. 780, 1903 ; M. le Blanc and E. Bindschedler, *ib.*, **8**. 260, 1902 ; W. Borchers, *ib.*, **3**. 484, 1897 ; W. Hempel and C. Schubert, *ib.*, **18**. 729, 1912 ; G. Just, *ib.*, **9**. 548, 1903 ; P. L. Dulong, *Journ. Mines*, **33**. 452, 1813 ; T. Göbel, *Chem. Ztg.*, **23**. 543, 1899 ; C. Reichard, *ib.*, **27**. 924, 943, 1903 ; J. Milbauer, *ib.*, **40**. 587, 1916 ; J. Milbauer and K. Kohn, *ib.*, **46**. 1146, 1922 ; *Ber. Böhm. Ges.*, 26, 1914 ; *Zeit. phys. Chem.*, **91**. 410, 1916 ; M. Faraday, *Quart. Journ. Science*, **19**. 155, 1926 ; A. A. Hayes, *Amer. Journ. Science*, (2), **20**. 409, 1855 ; E. L. Nichols, *ib.*, (3), **28**. 345, 1884 ; E. L. Nichols and B. W. Snow, *Phil. Mag.*, (5), **32**. 423, 1891 ; P. Grouvelle, *Ann. Chim. Phys.*, (2), **17**. 349, 1841 ; E. Duvillier, *ib.*, (4), **30**. 204, 1873 ; *Compt. Rend.*, **76**. 1353, 1873 ; H. Moissan, *ib.*, **98**. 1583, 1884 ; H. Moissan and P. Lebeau, *Ann. Chim. Phys.*, (7), **26**. 149, 1902 ; L. N. Vauquelin, *ib.*, (1), **70**. 70, 1809 ; S. M. Godon de St. Menin, *ib.*, (1), **53**. 222, 1805 ; *Ann. Musée Hist. Nat.*, **4**. 238, 1804 ; *Phil. Mag.*, **20**. 266, 1805 ; J. F. L. Hausmann, *Handbuch der Mineralogie*, Göttingen, 1847 ; W. Haidinger, *Handbuch der bestimmenden Mineralogie*, Wien, 1845 ; E. F. Glocker, *Gründriss der Mineralogie*, Nürnberg, 612, 1839 ; J. D. Dana, *A System of Mineralogy*, New York, 915, 1892 ; A. Breithaupt, *Berg. Hütt. Ztg.*, **17**. 54, 1858 ; F. Paneth and W. Vorwerk, *Zeit. phys.*

Chem., **101**. 445, 480, 1922 ; F. Paneth and W. Thimann, *Ber.*, **57**. B, 1215, 1924 ; F. Paneth, *Phys. Zeit.*, **15**. 924, 1914 ; E. Rutherford and F. Soddy, *Phil. Mag.*, (6), **4**. 58, 1902 ; (6), **5**. 445, 1903 ; P. B. Ganguly, *Journ. Phys. Chem.*, **31**. 481, 1927 ; E. Berger and L. Delmas, *Bull. Soc. Chim.*, (4), **29**. 68, 1921 ; J. N. Mukherjee and H. L. Ray, *Journ. Indian Chem. Soc.*, **1**. 173, 1924 ; V. Moravek, *Spisy Prirodovedeckou Fakulton Masarykovy Univ.*, 59, 1925 ; J. W. Bain, *Trans. Roy. Soc. Canada*, (3), **17**. 83, 1923 ; G. I. Pokrowsky, *Zeit. Physik.*, **36**. 473, 1926 ; **37**. 722, 1926 ; L. Kahlenberg and W. J. Trautmann, *Trans. Amer. Electrochem. Soc.*, **39**. 377, 1921 ; A. C. Chatterji and N. R. Dhar, *Zeit. anorg. Chem.*, **159**. 186, 1926 ; T. W. Case, *Phys. Rev.*, (2), **9**. 305, 1917 ; E. F. Chirva, *Trav. Musée Min. Acad., U.R.S.S.*, **1**. 43, 1926 ; M. W. Lomonossoff, *Metallurgy*, St. Petersburg, **1**. 44, 1763 ; I. M. Kolthoff, *Pharm. Weekbl.*, **57**. 934, 1920 ; J. Badams, *Ann. Phil.*, **25**. 303, 1825 ; J. B. Charcot and P. Yvon, *Journ. Pharm. Chim.*, (6), **5**. 379, 1897 ; P. Breteau and P. Fleury, *ib.*, (7), **10**. 265, 1914 ; K. B. Lehmann, *Arch. Hyg.*, **16**. 315, 1893 ; K. Jablczynsky, *Chem. Ind.*, **31**. 731, 1908 ; H. W. Hofmann, *Berichte über die Entwickelung der chemischen Industrie*, Braunschweig, **2**. 730, 1875 ; L. Bock, *Farben. Ztg.*, **25**. 625, 1920 ; G. Zerr, *ib.*, **17**. 132, 1911 ; G. Zerr and G. Rübencamp, *Handbuch der Farbenfabrikation*, Berlin, 354, 1909 ; London, 137, 1908 ; F. Rose, *Die Mineralfarben*, Leipzig, 335, 1916 ; J. G. Gentele, *Lehrbuch der Farbenfabrikation*, Braunschweig, **2**. 176, 1909 ; E. Guignet, *Fabrication des couleurs*, Paris, 101, 1888 ; A. de Gramont, *Analyse spectrale directe des minéraux*, Paris, 1895 ; *Bull. Soc. Min.*, **18**. 363, 1895 ; A. des Cloizeaux, *ib.*, **5**. 103, 1882 ; N. von Kokscharoff, *Materialien zur Mineralogie Russlands*, St. Petersburg, **7**. 95, 1875 ; W. H. Miller, *Introduction to Mineralogy*, London, 557, 1852 ; A. Kutzelnigg, *Ber.*, **63**. B, 1753, 1930 ; W. Ackroyd, *Chem. News*, **34**. 75, 1876 ; E. J. Houston and E. Thomson, *ib.*, **24**. 177, 188, 1871 ; M. Dullo, *Deut. Illustr. Gewerbeztg.*, **30**. 272, 1865 ; C. Schubert, *Beiträge zur Kenntnis der Dissoziation einiger Oxyde, Karbonate und Sulfide*, Weida i. Th., 37, 1910 ; J. Bersch, *Die Fabrikation der Erdfarben*, Wien, 1893 ; London, 186, 1901 ; G. H. Hurst, *Colour*, London, 1900 ; C. H. D. Bödeker, *Die Beziehungen zwischen Dichte und Zusammensetzung bei festen und liquiden Stoffen*, Leipzig, 1860 ; L. Playfair and J. P. Joule, *Mem. Chem. Soc.*, **2**. 401, 1845 ; P. Harting, *Bull. Sciences Néerl.*, **2**. 164, 1841 ; *Journ. prakt. Chem.*, (1), **22**. 52, 1841 ; J. Coneybeare, *Edin. Phil. Journ.*, **7**. 109, 1822 ; R. H. Brett, *Phil. Mag.*, (3), **10**. 95, 1837 ; J. A. Atanasiu, *Journ. Chim. Phys.*, **23**. 501, 1926 ; J. Spiller, *Journ. Chem. Soc.*, **10**. 110, 1858 ; *Chem. News*, **8**. 280, 1863 ; **19**. 166, 1869 ; E. C. Franklin and C. A. Kraus, *Amer. Chem. Journ.*, **20**. 828, 1898 ; A. Naumann, *Ber.*, **37**. 4329, 1904 ; R. Weinland and R. Stroh, *ib.*, **55**. B, 2706, 1922 ; K. Fajans and K. von Beckerath, *Zeit. phys. Chem.*, **97**. 478, 1921 ; P. W. Bridgeman, *Amer. Journ. Science*, (5), **10**. 483, 1925 ; E. R. Riegel and L. Widgoff, *Journ. Phys. Chem.*, **29**. 872, 1925 ; S. C. Bradford, *Science*, (2), **54**. 463, 1921 ; T. M. Lowry and L. P. McHatton, *Trans. Faraday Soc.*, **18**. 23, 1922 ; E. E. Free, *Journ. Phys. Chem.*, **13**. 126, 1909 ; J. F. G. Hicks, *ib.*, **25**. 545, 1921 ; J. F. G. Hicks and W. A. Craig, *ib.*, **26**. 563, 1922 ; C. Lückow, *German Pat., D.R.P.* 91707, 1894 ; 105143, 1895 ; *Brit. Pat. No.* 14801, 1895 ; J. Kronen, *ib.*, 19732, 1906 ; S. Ganelin, *ib.*, 8981, 1896 ; J. J. W. Watson and T. Slater, *ib.*, 595, 1852 ; F. G. Kidd, *ib.*, 134313, 1918 ; J. Massignon and E. Watel, *ib.*, 2224, 1891 ; D. G. Fitzgerald and R. C. Molloy, *ib.*, 2102, 1873 ; H. Hetherington and W. A. Allsebrook, *ib.*, 182693, 1921 ; H. N. Holmes, *Journ. Franklin Inst.*, **184**. 743, 1917 ; E. F. Anthon, *Repert. Pharm.*, **76**. 129, 1836 ; **81**. 358, 1846 ; P. Jannasch, *Ber.*, **22**. 221, 1889 ; **26**. 500, 1893 ; K. Preis and B. Rayman, *ib.*, **13**. 342, 1880 ; O. Meyer, *ib.*, **36**. 1743, 1903 ; H. G. F. Schröder, *ib.*, **11**. 2019, 1878 ; W. Autenrieth, *ib.*, **35**. 2063, 1902 ; H. C. Bolton, *ib.*, **13**. 733, 1880 ; L. Dede and P. Bonin, *ib.*, **55**. 2327, 1922 ; R. E. Liesegang, *Koll. Zeit.*, **12**. 74, 1913 ; E. Hatschek, *ib.*, **10**. 124, 1913 ; **14**. 115, 1914 ; **37**. 297, 1925 ; *Science Progress*, **17**. 86, 1922 ; *Proc. Roy. Soc.*, **99**. A, 496, 1922 ; E. Toelle and M. Hofe, *German Pat., D.R.P.* 186972, 1905 ; B. Redlich, *ib.*, 117148, 1899 ; R. Eberhard, *ib.*, 245165, 1910 ; B. Huick, *ib.*, 230826, 1909 ; M. Bamberger and R. Grengg, *Centr. Min.*, 65, 1921 ; B. Legg, *French Pat. No.* 429895, 1911 ; W. W. Coblentz, *Journ. Franklin Inst.*, **174**. 548, 1912 ; K. Toabe, *U.S. Pat. No.* 1225374, 1916 ; C. L. Parsons, *ib.*, 1239125, 1917 ; K. Haushofer, *Mikroskopische Reaktionen*, Braunschweig, 29, 1885 ; G. M. Schwab and E. Pietsch, *Zeit. phys. Chem.*, **2**. B, 262, 1929 ; A. Eisner, *Ueber den kinetischen Austausche an der Oberfläche natürlicher und künstlicher Kristalle*, Berlin, 1926 ; G. Cesaro, *Bull. Acad. Belg.*, 327, 1905 ; F. W. O. de Coninck, *ib.*, 508, 665, 1909 ; A. Baumann, *Zeit. angew. Chem.*, **4**. 328, 1891 ; H. Amsel, *ib.*, **9**. 613, 1896 ; H. Mennicke, *Zeit. öffentlich, Chem.*, **6**. 245, 1900 ; M. Tarugi, *Gazz. Chim. Ital.*, **29**. i, 512, 1899 ; C. Immerwahr, *Beiträge zur Löslichkeitsbestimmung schwerlöslicher Salze des Quecksilbers, Kupfers, Bleis, Cadmiums und Zinks*, Breslau, 1900 ; *Zeit. Elektrochem.*, **7**. 480, 1901 ; K. Ando, *Biochem. Journ.*, **9**. 215, 1928 ; H. Moser, *Chemische Abhandlung uber das Chrom*, Wien, 1824 ; *Schweigger's Journ.*, **42**. 99, 1824 ; A. Scheurer, *Bull. Soc. Mulhouse*, **54**. 364, 1884 ; H. H. Willard and J. L. Kassner, *Journ. Amer. Chem. Soc.*, **52**. 2402, 1930 ; M. A. Iljinsky and V. V. Kozloff, *Journ. Russ. Phys. Chem. Soc.*, **62**. 665, 1930 ; O. Ruff and E. Ascher, *Zeit. anorg. Chem.*, **185**. 369, 1930 ; O. Ruff, *ib.*, **185**. 387, 1930 ; Z. Karaoglanoff and B. Sagortschaff, *ib.*, **194**. 151, 1930 ; B. Gossner and F. Mussgnug, *Zeit. Kryst.*, **75**. 410, 1930 ; J. R. Campbell and T. Gray, *Journ. Soc. Chem. Ind.*, **49**. 450, T, 1930 ; D. N. Ghosh, *Journ. Indian Chem. Soc.*, **7**. 509, 1930.

[26] W. Schmid, *Beiträge zur Kenntnis der Chromate des Blei, Zink, Cadmium, und Wismuth*, Stuttgart, 1892 ; A. J. Cox, *Journ. Amer. Chem. Soc.*, **28**. 1694, 1906 ; *Ueber basische Quecksilbersalze*, Leipzig, 1904 ; *Zeit. anorg. Chem.*, **50**. 226, 1906 ; E. Rupp and G. Schaumann, *ib.*, **32**. 362, 1902 ; J. Löwe, *Journ. prakt. Chem.*, (1), **67**. 288, 463, 1856 ; M. M. P. Muir, *Journ. Chem. Soc.*, **29**. 483, 1876 ; **30**. 1876 ; **31**. 25, 645, 1877 ; R. W. Pearson, *Phil. Mag.*, (4), **11**. 204, 1856 ;

F. Nolle, *Liebig's Ann.*, **2**. 94, 1832 ; K. Preis and B. Rayman, *Sitzber. Böhm. Ges.*, 507, 1879 ; A. Naumann, *Ber.*, **37**. 4329, 1904 ; J. Milbauer, *Chem. Ztg.*, **40**. 587, 1916 ; S. H. C. Briggs, *Journ. Chem. Soc.*, 242, 1929.

[27] C. W. Blomstrand, *Acta Lund. Univ.*, **1**. 7, 1864 ; **2**. 3, 1865 ; *Journ. prakt. Chem.*, (1), **99**. 44, 1866 ; *Liebig's Ann.*, **135**. 198, 1865 ; H. J. S. King, *Journ. Chem. Soc.*, **125** 1329, 1924 ; **127**. 2100, 1925.

[28] O. T. Christensen, *Journ. prakt. Chem.*, (2), **24**. 86, 1881 ; S. M. Jörgensen, *ib.*, (2), **20**. 143, 1879 ; (2), **25**. 91, 1882 ; (2), **45**. 271, 1892 ; P. T. Cleve, *Lärobok i oorganisk Kemi*, Stockholm, 1873 ; P. Pfeiffer and W. Vorster, *Zeit. anorg. Chem.*, **58**. 296, 1908 ; A. Hiendlmayr, *Beiträge zur Chemie der Chrom- und Kobalt-Ammoniake*, Freising, 1907 ; E. Wilke-Dörfurt and K. Niederer, *Zeit. anorg. Chem.*, **184**. 145, 1929 ; W. J. Sell, *Proc. Roy. Soc.*, **33**. 267, 1882 ; **45**. 321, 1889.

[29] J. J. Berzelius, *Pogg. Ann.*, **6**. 384, 1826 ; J. F. John, *Schweigger's Journ.*, **3**. 378, 1811 ; *Gehlen's Journ.*, **3**. 452, 1804 ; **4**. 434, 1804 ; J. Formanek, *Böhm. Pharm. Ztg.*, **12**. 117, 1880 ; *Liebig's Ann.*, 257, 102, 1890 ; J. Wiesner, *Anz. Böhm. Naturf. Vers.*, 61, 1882 ; E. Rimbach, *Ber.*, **37**. 461, 1904 ; H. Bürger, *Beiträge zur Kenntnis der Uranyldoppelsalze*, Bonn, 50, 1904 ; J. Aloy, *Compt. Rend.*, **122**. 1541, 1896 ; N. A. Orloff, *Chem. Ztg.*, **31**. 375, 1907 ; H. Moser, *Chemische Abhandlung über das Chrom*, Wien, 1824 ; *Schweigger's Journ.*, **42**. 99, 1824 ; C. F. Rammelsberg, *Pogg. Ann.*, **55**. 318, 1842 ; **56**. 125, 1842 ; **59**. 1, 1843 ; *Ber.*, **5**. 1003, 1872 ; S. H. C. Briggs, *Zeit. anorg. Chem.*, **56**. 246, 1907 ; B. Szilard, *Zeit. wiss. Photochem.*, **4**. 350, 1906 ; A. Atterberg, *Akad. Afhandl. Upsala*, 1872 ; *Nägra Bidrag till kennedomen om Molybdän*, Upsala, 1872.

[30] T. Thomson, *Ann. Phil.*, **16**. 321, 1820 ; P. Grouvelle, *Ann. Chim. Phys.*, (2), **17**. 349, 1821 ; J. F. John, *Schweigger's Journ.*, **3**. 378, 1811 ; *Gehlen's Journ.*, **3**. 452, 1804 ; **4**. 436, 1804 ; R. Warington, *Phil. Mag.*, (3), **21**. 380, 1842 ; U. Antony and U. Paoli, *Gazz. Chim. Ital.*, **32**. i, 518, 1902—from *Journ. Chem. Soc.*, **82**. ii, 661, 1902 ; E. Schulze, *Zeit. anorg. Chem.*, **10**. 154, 1895 ; M. Gröger, *ib.*, **44**. 459, 1905 ; C. Freese, *Pogg. Ann.*, **140**. 253, 1870 ; H. Reinsch, *ib.*, **55**. 97, 1842 ; A. J. Fairrie, *Journ. Chem. Soc.*, **4**. 300, 1851 ; C. Hensgen, *Rec. Trav. Chim. Pays-Bas*, **4**. 212, 1885 ; F. Breinl and J. Klaudy, *Mitt. Tech. Gewerbemus. Wien*, (2), **1**. 55, 1878 ; E. Donath, *Dingler's Journ.*, **264**. 48, 1887.

[31] L. N. Vauquelin, *Ann. Chim. Phys.*, (1), **70**. 70, 1809 ; A. Maus, *Pogg. Ann.*, **9**. 127, 1827 ; **11**. 83, 1827 ; C. W. Eliot and F. H. Storer, *Proc. Amer. Acad.*, **5**. 207, 1862 ; *Chem. News*, **6**. 121, 136, 145, 157, 169, 182, 207, 217, 1862 ; C. Hensgen, *Ber.*, **12**. 1300, 1656, 1879 ; R. Weinland and E. Mergenthaler, *ib.*, **57**. 8, 776, 1924 ; S. H. C. Briggs, *Journ. Chem. Soc.*, 242, 1929 ; V. Kletzinsky, *Dingler's Journ.*, **207**. 83, 1873 ; C. Lepierre, *Compt. Rend.*, **119**. 1215, 1894 ; L. Blanc, *Ann. Chim. Phys.*, (10), **6**. 182, 1926 ; *Étude de quelques transformations observées au cours de la calcination des sesquioxydes de fer, de chrome et d'aluminium*, Paris, 1926 ; L. A. Wels, *Phil. Mag.*, (7), **6**. 481, 1928.

[32] F. J. Malaguti and M. Sarzeau, *Ann. Chim. Phys.*, (3), **7**. 431, 1843 ; C. Freese, *Pogg. Ann.*, **140**. 253, 1869 ; F. de Boer, *Arch. Neerl.*, (3), **5**. 101, 1927 ; J. Schulze, *Zeit. anorg. Chem.*, **10**. 154, 1895 ; M. Gröger, *ib.*, **49**. 196, 1906 ; **58**. 412, 1908 ; S. M. Jörgensen, *ib.*, **5**. 167, 1894 ; *Journ. prakt. Chem.*, (2), **18**. 234, 1878 ; (2), **19**. 66, 1879 ; (2), **23**. 245, 1881 ; (2), **42**. 216, 1890 ; C. D. Braun, *Untersuchungen über ammoniakalische Kobaltverbindungen*, Göttingen, 1862 ; *Liebig's Ann.*, **125**. 184, 1863 ; O. W. Gibbs, *Amer. Journ. Science*, (2), **37**. 57, 1864 ; *Proc. Amer. Acad.*, **10**. 8, 1875 ; **11**. 28, 1876 ; O. W. Gibbs and F. A. Genth, *Researches on the Ammonia-cobalt Bases*, Washington, 44, 1856 ; *Amer. Journ. Science*, (2), **23**. 249, 320, 1857 ; *Journ. prakt. Chem.*, (1), **72**. 163, 1857 ; T. Klobb, *Bull. Soc. Chim.*, (3), **25**. 1022, 1901 ; G. Vortmann, *Ber.*, **15**. 1894, 1882 ; S. H. C. Briggs, *Zeit. anorg. Chem.*, **56**. 247, 1908 ; **63**. 325, 1909 ; *Journ. Chem. Soc.*, **115**. 67, 1919 ; 242, 1929 ; 685, 1929 ; N. Parravano and A. Pasta, *Gazz. Chim. Ital.*, **37**. ii, 259, 1907 ; A. Hiendlmayr, *Beiträge zur Chemie der Chrom- und Kobalt-Ammoniake*, Freising, 1907 ; J. N. Brönsted and A. Petersen, *Journ. Amer. Chem. Soc.*, **43**. 2265, 1921 ; P. R. Ray and P. V. Sarkar, *Journ. Indian Chem. Soc.*, **1**. 289, 1925 ; P. R. Ray, *ib.*, **4**. 64, 1927.

[33] F. J. Malaguti and M. Sarzeau, *Ann. Chim. Phys.*, (3), **9**. 431, 1843 ; R. Tupputi, *ib.*, (1), **78**. 133, 1811 ; (1), **79**. 153, 1811 ; H. Stokes, *Phil. Mag.*, (2), **2**. 427, 1827 ; *Quart. Journ. Science*, **2**. 477, 1827 ; C. Freese, *Pogg. Ann.*, **140**. 250, 1870 ; E. A. Schmidt, *Liebig's Ann.*, **156**. 19, 1870 ; J. F. John, *Schweigger's Journ.*, **3**. 378, 1811 ; *Gehlen's Journ.*, **3**. 452, 1804 ; **4**. 436, 1804 ; M. Gröger, *Zeit. anorg. Chem.*, **51**. 352, 1906 ; S. H. C. Briggs, *Proc. Chem. Soc.*, **18**. 254, 1902 ; **20**. 90, 1904 ; *Journ. Chem. Soc.*, **85**. 678, 1904 ; 242, 1929 ; *Zeit. anorg. Chem.*, **56**. 247, 1908 ; **63**. 325, 1909 ; G. L. Clark, *Amer. Journ. Science*, (5), **7**. 14, 1924.

[34] P. T. Cleve, *Acta Univ. Upsala*, **6**. 61, 1866 ; S. G. Hedin, *Om pyridinens platinabaser*, Lund, 1885 ; C. Enebuske, *Om platinas methylsulfinbaser*, Lund, 1885 ; T. Thomson, *Ann. Phil.*, **16**. 321, 1820 ; G. B. Buckton, *Journ. Chem. Soc.*, **5**. 213, 1852.

§ 16. The Dichromates

H. Moser,[1] Y. T. Gerassimoff, and others obtained **ammonium dichromate,** $(NH_4)_2Cr_2O_7$, by evaporating a soln. of chromic acid half sat. with ammonia. Y. T. Gerassimoff said that double decomposition with ammonium chloride and sodium dichromate gives an impure product. S. Darby, J. S. Abel, and J. S. Abel and H. Richmond showed that if the chromic acid is contaminated with sulphuric acid, that salt is easily freed from that contamination by recrystallization. R. Segalle obtained ammonium dichromate by heating an ammoniacal soln. of a mol of potassium dichromate until the liquid has a garnet-red colour; and then evaporating for crystallization. F. A. H. Schreinemakers' observations on the equilibrium conditions are summarized in Fig. 29. Analyses were reported by S. Darby, M. Gröger, M. Siewert, J. Schabus, and J. S. Abel and H. Richmond.

The yellowish-red crystals were found by C. F. Rammelsberg to be monoclinic prisms with the axial ratios $a : b : c = 1\cdot0271 : 1 : 1\cdot7665$, and $\beta = 93^\circ 42'$. The (101)-cleavage is clear, and the (010)-cleavage incomplete. Observations on the crystals were also made by H. J. Brooke, J. Schabus, and A. J. Weiss. G. N. Wyrouboff noted some resemblances between the crystals and those of triclinic potassium dichromate; but the two salts are not isomorphous. B. Gossner and F. Mussgnug found that the X-radiograms showed that the monoclinic crystals have a cell with $a = 7\cdot78$ A., $b = 7\cdot54$ A., and $c = 13\cdot27$ A., with $\beta = 93^\circ 42'$. Unit cell contains 4 mols. A. Duffour said that the crystals are isomorphous with the monoclinic form of potassium dichromate. H. Schiff gave 2·367 for the sp. gr.; F. W. Clarke, and G. N. Wyrouboff, 2·150; and E. Moles and F. Gonzalez, 2·16 at 25°. K. F. Slotte found the sp. gr. of soln. of ammonium dichromate with 6·85, 13·0, and 19·93 per cent. of the dichromate to be respectively 1·0393, at 12°, 1·0782 at 10·5° and 1·1258 at 12°; and the viscosities (water 100) to be respectively 98·9, 99·1, and 100·6 at 10°; 76·8, 78, 80·2, at 20°; 62·5, 63·9 and 66·4 at 30°; and 51·9, 53·3, and 55·7 at 40°. H. Moser, and E. Jäger and G. Krüss said that the salt is stable in air; and J. S. Abel and H. Richmond, that it is stable at 100°. A. Maus, R. Böttger, E. Moles and F. Gonzalez, and A. A. Hayes found that the salt decomposes at a temp. below redness leaving a residue of chromic oxide. The reaction is attended by the emission of light, and may be by a feeble detonation, especially, as shown by M. Siewert, if it be quickly heated in a test-tube. The gaseous products of the reaction were found by J. S. Abel and H. Richmond, and A. Levy to be nitrogen and water, but S. Darby observed that some ammonia gas may be produced; and M. Siewert, and W. M. Hooton, some nitric oxide and oxygen. C. N. Hinshelwood and E. J. Bowen studied the rate of decomposition at 219°. W. C. Ball said that at 185°–205° the salt darkens in colour, and decomposes slowly with the evolution of water, nitrogen, and ammonia; and after six days' heating, there remains a black residue approximating $3CrO_2.H_2O$; and if the heating be interrupted when the salt is half decomposed, an insoluble black product, approximating $Cr_2O_3.2CrO_3.2NH_3.H_2O$, is obtained. W. M. Hooton found that if ammonium dichromate be heated in air, below the inflammation temp. 190°, the end-product has the composition $2CrO_2.H_2O$; and if heated in the absence of oxygen, $H_2Cr_2O_4$—*vide supra* for E. Maumené's observations on ammonium chromate. E. Moles and F. Gonzalez observed that tranquil decomposition occurs at about 225°, and that the oxidation of the "ammonium" to nitrogen is most complete where the reaction occurs most rapidly. The black residue thereby obtained is chromium peroxide. Y. T. Gerassimoff found that the aq. soln. is slightly decomposed when it is boiled.

R. Böttger said that if an intimate mixture of the dichromate with half its weight of picric acid be brought in contact with a glowing splint, it decomposes with sparking forming pale green, flocculent chromic oxide. C. N. Hinshelwood and E. J. Bowen studied the rate of the thermal decomposition of ammonium dichromate. With the explosive decomposition of the salt, M. Berthelot found that 7·8 Cals. are developed; and he gave for the heat of formation: $2H_2CrO_4(800_{aq.}) + 2NH_4OH(1600_{aq.}) = (NH_4)_2Cr_2O_{7aq.} + 24$ Cals at 12°; E. Moles and F. Gonzalez, 23·275 Cals., and F. Morges, 26·988 Cals. at 19·5°. M. Berthelot gave for the reaction $(NH_4)_2Cr_2O_{7aq.} + 2NH_4OH_{aq.} = 2(NH_4)_2CrO_{4aq.} + 20\cdot4$ Cals.; for precipitated chromic oxide, $2Cr(OH)_3 + 2NH_4OH_{aq.} + 3O = (NH_4)_2Cr_2O_{4aq.} + 34\cdot6$ Cals. at 12°; and 47

Cals. with the solid dichromate; $(NH_4)_2CrO_{4\text{solid}}+CrO_{3\text{solid}}=(NH_4)_2Cr_2O_{7\text{solid}}+11\cdot300$ Cals. For the heat of decomposition, $(NH_4)_2Cr_2O_7=Cr_2O_3+N_2+4H_2O+(78\cdot000+Q)$ cals., where Q denotes the heat of transformation of chromic oxide. For the reducing action of ammonia on chromium trioxide: $2CrO_3+2NH_3=Cr_2O_3+3H_2O_{\text{gas}}+N_2+146\cdot6$ Cals.; the heat of soln. of a mol of the salt in 560 mols of water at 13° is $-12\cdot44$ Cals.; E. Moles and F. Gonzalez gave $-12\cdot904$ Cals.; P. Sabatier gave $-5\cdot8$ Cals. for the heat of soln. of a mol of the salt in 200 mols of water. P. Sabatier measured the absorption spectrum. S. Schlivitch observed a photovoltaic effect with soln. of ammonium dichromate and platinum electrodes. H. Moser said that the aq. soln. has a saline taste, and reddens litmus. The salt is less soluble than ammonium chromate. E. Moles and F. Gonzalez gave for the solubility 23·88 per cent. at 16°, and 28·63 per cent. at 25°. F. A. H. Schreinemakers found that 100 grms. of water at 30° dissolve 47·17 grms. of ammonium dichromate. The salt in aq. soln. is less hydrolyzed than the monochromate, and Y. T. Gerassimoff found that the solubilities of ammonium dichromate, S grms. of salt per 100 grms. of water, working on cooling and heating systems, are:

		0°	20°	40°	60°	80°	100°
S	Cooling .	18·40	36·0	58·7	86·0	—	—
	Heating .	18·13	35·3	58·4	86·0	115·0	155·6

and the disturbance is probably due to undercooling. The solubility curves for the system $(NH_4)_2Cr_2O_7$–$(NH_4Cl)_2$–H_2O at different temp., are summarized in Fig. 65—mols of salt per 1000 mols of water; *confer* Fig. 1, **1**. 11, 1. A. Naumann and A. Rücker calculated that in a N-soln. at the b.p., 0·0108 per cent. is hydrolyzed. B. Reinitzer said that the salt is soluble in absolute alcohol. W. P. Jorissen discussed the limits of the reaction of ammonium dichromate with potassium chloride and sulphate.

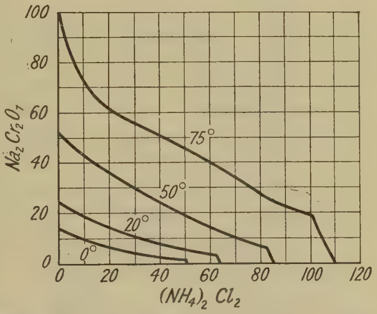


FIG. 65.—The Effect of Ammonium Chloride on the Solubility of Ammonium Dichromate.

According to C. F. Rammelsberg,[2] if chromic acid or nitric acid be added to a soln. of lithium chromate, the liquid furnishes deliquescent crystals of **lithium dichromate,** $Li_2Cr_2O_7.2H_2O$. The conditions of equilibrium are illustrated by Fig. 31. The black plates have curved surfaces. L. Schulerud found that the water of crystallization is completely lost at 130°, and the salt melts at a higher temp. with the evolution of oxygen. The salt can be recrystallized from water without decomposition; and F. A. H. Schreinemakers observed that 100 grms. of water at 30° dissolve 130·4 grms. of $Li_2Cr_2O_7$. A. Heydweiller found the sp. gr., and eq. conductivity, at 18°, to be:

	0·2N-	0·5N-	N-	2N-
Sp. gr. . .	1·01581	1·03928	1·0780	1·1540
λ . . .	73	66·1	58·7	47·7

The preparation of **sodium dichromate,** $Na_2Cr_2O_7.2H_2O$, is effected by methods similar to those employed for the potassium salt. J. d'Ans and J. Löffler[3] observed it amongst the products of the action of sodium hydroxide on chromic oxide. M. Siewert said that it is not produced by partially saturating sodium chromate with nitric acid, but it is produced by dissolving sodium chromate in a slight excess of chromic acid, and evaporating the liquid over sulphuric acid in vacuo. G. Bessa discussed the manufacture of sodium dichromate. R. Kissling found that commercial samples contained 83·79 to 92·84 per cent. $Na_2Cr_2O_2$; and with seven different samples, 23 days' exposure resulted in the absorption of 60 per cent. of water in each case. B. Neumann and C. Exssner discussed the conversion of sodium chromate to dichromate in aq. soln. by carbon dioxide under press.

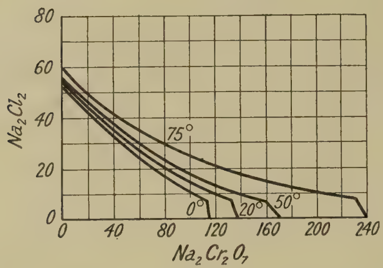


FIG. 66.—The Effect of Sodium Chloride on the Solubility of Sodium Dichromate.

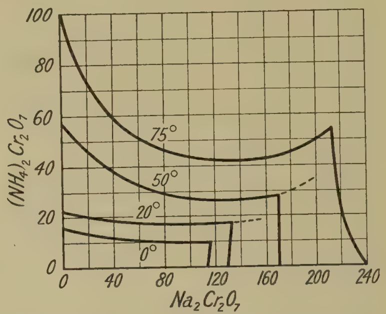


FIG. 67.—The Effect of Ammonium Dichromate on the Solubility of Sodium Dichromate.

E. Müller and E. Sauer found that in the conversion of soln. of sodium chromate to dichromate and hydroxide by electrolysis, if the anolyte is a soln. of sodium chromate and the catholyte one of sodium hydroxide the yield is less than if sodium chromate is used in both compartments. A. Lottermoser and K. Falk found that better yields are obtained with three compartment cells with sodium chromate in all three compartments rather than with sodium hydroxide as catholyte and sodium chromate in the other two compartments. This is because in the former case circumstances are least favourable for the migration of HO-ions into the anode compartment. I. Stsherbakoff studied the electrolysis of soln. of sodium chromate using a mercury cathode. T. W. Richards and G. L. Kelley found that sodium dichromate can be readily purified from potassium salts and sulphates by recrystallization from water a number of times. The conditions of equilibrium, worked out by F. A. H. Schreinemakers, are illustrated by Fig. 34. F. Mylius and R. Funk gave 83° for the transition temp. from the *dihydrate* to the anhydrous salt. The solubility, *S* per cent., of sodium dichromate in water is :

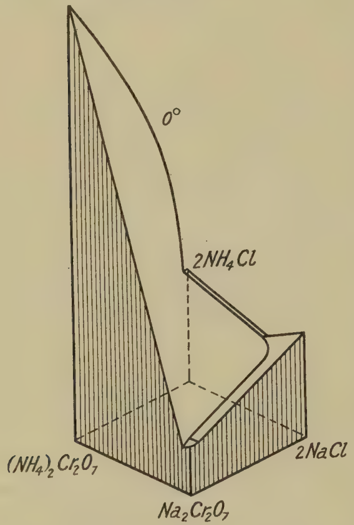


FIG. 68.—The Quaternary System : $(NH_4)_2Cr_2O_7$–$Na_2Cr_2O_7$–Na_2Cl_2–$(NH_4Cl)_2$ at 0°.

	0°	10°	20°	40°	60°	80°	83°	93°	98°
S .	62·0	63·0	64·3	68·8	73·9	79·4	80·7	81·20	81·24
Solid phase	$Na_2Cr_2O_7.2H_2O$						$Na_2Cr_2O_7$		

A. Stanley found that 100 parts of water dissolve 107·2 parts of $Na_2Cr_2O_7$ at 0° ; 109·2 parts at 15° ; 116·6 parts at 30° ; 142·8 parts at 80° ; 162·8 parts at 100° ; and 209·7 parts at 139°. F. A. H. Schreinemakers found that at 30° water dissolves 66·4 per cent. of $Na_2Cr_2O_7$. Y. I. Gerassimoff found that the solubility curves for the system $Na_2Cr_2O_7$–NaCl–H_2O, at different temp., are summarized in Fig. 66—mols of salt per 100 mols of water—*confer* Fig. 1, **1**. 11, 1. The solubility curves for the system $(NH_4)_2Cr_2O_7$–$Na_2Cr_2O_7$–H_2O, at different temp., are summarized in Fig. 67—mols of salt per 1000 mols of water—*confer* Fig. 1, **1**. 11, 1. The equilibrium diagrams for the quaternary systems $(NH_4)_2Cr_2O_7$–$Na_2Cr_2O_7$–Na_2Cl_2–$(NH_4Cl)_2$, at 0° and 75° are indicated in Figs. 68 and 69.

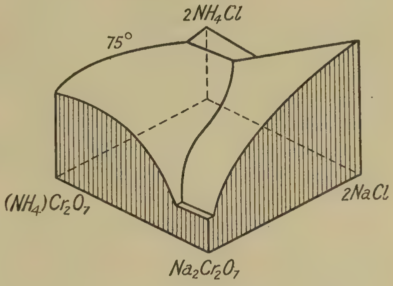


FIG. 69.—The Quaternary System: $(NH_4)_2Cr_2O_7$–$Na_2Cr_2O_7$–Na_2Cl_2–$(NH_4Cl)_2$ at 75°.

The dihydrate furnishes hyacinth-red, thin, six-sided prisms which, according to M. Siewert, are triclinic, but, according to L. Münzing, are monoclinic. G. N. Wyrouboff gave for the axial ratios of the monoclinic crystals $a:b:c=0{\cdot}5698:1:1{\cdot}824$, and $\beta=94°\ 55'$; while L. Münzing gave $0{\cdot}5912:1:0{\cdot}5698$, and $\beta=85°\ 5'$. The optic axial angle $2V=83°\ 54'$; and the optical character is positive. The deliquescent crystals were found by A. Stanley to have a sp. gr. 2·5246 at 13°. According to A. Stanley, the sp. gr. of the aq. soln. is:

$Na_2Cr_2O_7$.	1	5	10	20	30	40	50 per cent.
Sp. gr. . .	1·007	1·035	1·071	1·141	1·208	1·280	1·343

while H. C. Jones and H. P. Basset gave at 18°,

$Na_2Cr_2O_7$.	1·31	2·59	5·09	7·50	9·83	18·40	26·90 per cent.
Sp. gr. . .	1·0096	1·0190	1·0377	1·0568	1·0756	1·1491	1·2285

L. J. Simon measured the viscosities of soln. of sodium dichromate—*vide supra*, potassium chromate. F. Mylius and R. Funk observed that a soln. sat. at 18° contains 63·92 per cent. of $Na_2Cr_2O_7$, and has a sp. gr. 1·745; F. Rüdorff found that the salt does not decompose when in aq. soln. I. Traube found the drop-weight of the molten anhydrous salt to be 262·0 mgrms. A. Stanley found that the dihydrate becomes anhydrous above 303°; it melts at 320°, and decomposes at 400° with the evolution of oxygen. P. L. Robinson and co-workers observed no transition phenomenon when the salt is cooled between 300° and 70°. H. C. Jones and H. P. Bassett found that soln. with 0·1, 0·2, and 0·4 mols per litre lower the f.p. of water respectively 0·490°, 0·946°, and 1·872°. A. Stanley said that the sat. aq. soln. boils at 139°. J. Thomsen gave for the heat of formation: $2H_2CrO_4(800_{aq.})+2NaOH(400_{aq.})=Na_2Cr_2O_{7aq.}+26{\cdot}268$ Cals. at 18°; and F. Morges, $2H_2CrO_{4aq.}+2NaOH_{aq.}=Na_2Cr_2O_7+26{\cdot}076$ Cals. at 19·5°.

H. Dufet found the indices of refraction of the crystals of the dihydrate to be $\alpha=1{\cdot}7510$, $\beta=1{\cdot}6994$, and $\gamma=1{\cdot}6610$ for the D-line. P. Walden measured the electrical conductivity of aq. soln. at 25°; while H. C. Jones and co-workers found for the molar conductivity, μ mho, and for the percentage ionization, α, calculated from μ/μ_∞, with a mol of the salt in v litres of water:

	v . . .	8	16	32	128	512
μ	0° . .	92·18	96·57	101·25	106·8	106·1
	15° . .	136·5	143·5	148·4	158·3	158·3
	25° . .	—	176·3	182·7	194·7	194·4
	35° . .	—	211·4	219·5	233·5	234·6
α	0° . .	87·5	91·3	95·7	100·0	100·0
	35° . .	—	89·9	93·3	100·0	100·0

H. C. Jones calculated from the sp. gr., f.p., and conductivity data that soln. with M mols per litre have H mols of water in combination with a mol of the salt, when M is 0·1, 0·2, 0·3, and 0·4, H is respectively 20·5, 9·7, 6·5, and 7·9. A. Poirot found that the emission of anodic rays with purified sodium dichromate is regular and stable. The emission starts suddenly below the m.p. of the salt. The anode is surrounded by a yellowish glimmer. There is an intense yellow spot on the cathode where it is hit by the anodic rays. The spectra of the anodic and cathodic lights were examined. H. Ollivier studied Verdet's constant, and the paramagnetism of the salt. E. C. Franklin and C. A. Kraus said that the salt is insoluble in liquid ammonia; A. Naumann, that it is insoluble in acetone; and B. Reinitzer that 100 c.c. of a soln. in alcohol contain 5·13 grms. of $Na_2Cr_2O_7.2H_2O$. The alcoholic soln. decomposes rapidly. V. K. la Mer and C. L. Read found that the reaction between sodium hydroxide and dichromate is unimolecular with respect to the dichromate and the velocity constant is k=529 per min., and the heat of reaction 15,320 cals. per mol of dichromate. The results are best interpreted as involving the reactions: $Cr_2O_7'' + H_2O \rightleftharpoons 2HCrO_4'$ (slow), with $Q=-13,640$ cals. per mol $Cr_2O''_7$; $HCrO_4' \rightleftharpoons H^{\cdot} + CrO_4''$ (rapid), with $Q=780$ cals. per mol $HCrO_4'$; and $H^{\cdot} + OH' = H_2O$ (rapid).

The manufacture of **potassium dichromate,** $K_2Cr_2O_7$, has been discussed in connection with the extraction of chromium from chromite, etc. F. Tassaert[4] obtained it by mixing soln. of chromic acid and potassium hydroxide in such proportions that the soln. reacts neither acidic nor alkaline, and evaporating the liquid. The dichromate first separates out, and the mother-liquid, then reacting alkaline, furnishes the monochromate. It is also obtained from acidified soln. of potassium chromate. E. Gray, and V. S. Yatloff also described its preparation. The conditions of equilibrium have been studied by F. A. H. Schreinemakers, F. Flöttmann, and I. Koppel and E. Blumenthal, and the results are summarized in Figs. 36 to 41. Y. R. Goldstein, and H. Pincass discussed the transformation from chromate to dichromate by carbon dioxide; and I. Obreimoff and W. J. de Haas, the colour changes at low temp. The bright-red, rectangular, four-sided tabular or prismatic crystals are triclinic pinacoids which, according to J. Schabus, have the axial ratios $a:b:c=0·5575:1:0·5511$, and $\alpha=82° 0'$, $\beta=90° 51'$, and $\gamma=83° 47'$. The (010)-cleavage is perfect; and the (100)- and the (001)-cleavages are distinct. G. N. Wyrouboff also made some crystallographic observations. B. Gossner and F. Mussgnug showed that the X-radiograms of the triclinic salt correspond with a unit cell having 4 mols., and $a=7·50$ A., $b=7·38$ A., and $c=13·40$ A., whilst $\alpha=82° 0'$, $\beta=96° 13'$, and $\gamma=90° 51'$. H. Dufet observed that the optical character is positive; and that the optic axial angles $2E=98° 58'$ and $2V=51° 53'$ for the D-line; and $2V=52° 24'$ for the Li-line. A. Beer observed that the crystals are pleochroic. H. Baumhauer studied the corrosion figures. A. Schubnikoff showed that a crystal, suspended in a slighly supersaturated soln. rotating on a horizontal axis, grows so that the (001)-face is bright and smooth, while the $(00\bar{1})$-face is dull and rough, while the other parallel faces are not the same size or are absent. This is taken to show that the crystals of the dichromate belong to the asymmetric class of the triclinic system. A. Hettich and A. Schleede made observations on the crystals. E. Pietsch and co-workers found that the attack on the crystals by sulphuric acid begins at the corners and edges. D. N. Artemeéff, R. Marc, M. le Blanc and W. Schmandt, H. Jeannel, M. Kimura, and C. Tomlinson studied the growth of crystals in supersaturated soln. The rate of growth of the crystals is not solely a diffusion phenomenon as is the case with the speed of dissolution—*vide infra.* H. A. Miers said:

> If a drop of strong soln. of potassium dichromate, placed upon a microscope-slide, be observed under the microscope as it crystallizes, and if the drop be sufficiently thin, it will generally be found that the following events take place: The first crystals make their appearance at the edges of the drop and after growing rapidly for a short period as branching fibres, they begin to grow quietly in the form of plates or flattened rods presenting the characteristic form of the crystals of this substance. These crystals continue to grow uniformly, but after a short period, at a distance from the growing crystals, and at some spot where the drop is thin, a fresh crystalline growth starts suddenly from a point, and extends with great rapidity in all directions in the form again of branching needles and fibres. After a short period this rapid growth ceases and each of the fibres swells out at the end into a well-defined crystal and continues to grow slowly and uniformly as a single, regular plate. The process may be repeated by the sudden development of a new spontaneous growth in another portion of the drop, and the same succession of events may be repeated again and again. Sometimes these successive growths constitute a series of

rings approximately parallel to the edges of the drop which follow one another till the centre of the drop is reached.

An illustration of a drop of the dichromate in the act of crystallization is shown **1**. 11, 3, Fig. 11. The phenomenon connected with crystallizations in labile and metastable soln.—**1**. 9, 6, Fig. 14—gave a possible explanation for the periodic crystallization of soln. of potassium dichromate. E. Pietsch and co-workers studied the attack at the corners and edges of the crystals by conc. sulphuric acid, and by an ethereal soln. of hydrogen dioxide. W. von Behren and J. Traube studied the phenomenon attending the dissolution and crystallization of the salt. E. S. Hedges obtained spiral forms of rhythmic crystallization ; and E. N. Gapon studied the rate of crystallization.

Crystals appear at the edge of the drop where, owing to evaporation or cooling, the soln. is sufficiently strong to be in the labile condition, and proceed as rapidly growing fibres ; but so soon as these have by their growth reduced the strength of the soln. in their neighbourhood to the metastable state they continue to grow quietly and uniformly ; presently, however, at some point sufficiently distant from the growing crystals to be also in the labile state, crystallization starts afresh, either spontaneously or perhaps through inoculation by a crystalline speck falling into the drop from the air. This again proceeds as the rapid, fibrous growth, characteristic of the labile condition, until again the liquid passes into the metastable state and the growth is slow.

Soln. with 17·266 (28·5°), 20·00 (32·2°) and 29·09 (43·5°) grms. of salt in 100 parts of water, and sat. at the temp. named, were labile respectively at 18·5°, 22°, and 34°. M. Volmer and A. Weber discussed the formation of nuclei in undercooled soln. C. Decharne observed the crystallization of the dichromate from a soln. mixed with gum, when under the influence of a strong magnetic field. G. Brügelmann said that potassium dichromate forms isomorphous mixtures with pentahydrated cupric sulphate, but J. C. G. de Marignac did not agree. S. F. Schemtschuschny studied the formation of isomorphous mixtures with potassium chloride ; and C. F. Rammelsberg, P. Groth, L. Stibing, A. Sella, A. Fock, H. le Chatelier, and C. von Hauer, solid soln. with potassium pyrosulphate. C. von Hauer observed that the crystals of the dichromate take up potassium sulphate when that salt is present in the liquid during the crystallization.

Triclinic potassium dichromate may be called the α-form ; there is also a monoclinic β-form. E. Mitscherlich observed that when the molten dichromate is slowly cooled, crystals are formed which afterwards decrepitate ; O. Lehmann showed that the change is reversible ; G. Tammann found that there is a large change in vol. at 240°, accompanied by an imperceptible thermal change ; G. Tammann and Q. A. Mansuri measured the rate of crystallization of the powdered salt and found that it commences at 160° with particles over 1 mm. diam., at 166° with particles between 1·0 and 0·3 mm., and at 158·5°–163° with particles smaller than 0·3 mm., and G. N. Wyrouboff concluded that potassium dichromate exists in three forms : (i) a monoclinic form stable near the m.p. ; (ii) a triclinic form stable at the ordinary temp. ; and (iii) a second triclinic form stable in a narrow range of temp. between the other two forms. S. F. Schemtschuschny added that the transition temp., $\alpha\text{-}K_2Cr_2O_7=\beta\text{-}K_2Cr_2O_7$, is 236° ; and P. L. Robinson and co-workers gave 236·8°. P. L. Robinson and co-workers added that the salt separates from the fused state in a compact mass of dark brownish-red, tabular crystals with marked reduction in volume. On further cooling, the crystals change to a loose, orange-red powder. The existence of G. N. Wyrouboff's second triclinic form has not been confirmed, so that the crystals which first separate from the cooling liquid are doubly refracting—probably monoclinic, and at about 236° these crystals pass into the ordinary triclinic form. O. Hauser and H. Herzfeld observed that when hot, conc. soln. of potassium dichromate and hot potassium thiocyanate are mixed, the dichromate crystallizes on cooling in yellowish-brown, doubly-refracting, monoclinic plates. The sp. gr. of this form is 2·10, whereas that of the ordinary triclinic variety is 2·67. The monoclinic dichromate is unstable, and is transformed into the triclinic salt when kept in contact with its sat. soln., or in moist air. It seems probable that this form of the potassium salt is isomorphous with monoclinic ammonium dichromate. A. Duffour also observed that if a considerable excess of aluminium sulphate is added to a soln. of potassium monochromate, some aluminium hydroxide is precipitated, and when the soln. is concentrated by heat, potassium dichromate separates out in monoclinic and triclinic crystals. The monoclinic crystals are isomorphous with those of rubidium and ammonium dichromates. P. L. Stedehouder and P. Terpstra found for the monoclinic form $a:b:c=1{\cdot}0123:1:1{\cdot}7675$, and $\beta=88° 4{\cdot}5'$; and the optic axial angle of the pleochroic crystals $2V=66° 14'$. The X-radiograms gave $a=7{\cdot}42$ A., $b=7{\cdot}35$ A., $c=12{\cdot}97$ A., and $\beta=91° 55°$, with 4 mols. per unit cell which is face-centred on the (100)-side. According to A. Duffour, the axial ratios for the three forms are $a:b:c=1{\cdot}0167:1:1{\cdot}7716$, and $\beta=91° 55'$ for $K_2Cr_2O_7$; $1{\cdot}0202:1:1{\cdot}8081$, and $\beta=98° 28{\cdot}5'$ for $Rb_2Cr_2O_7$; and $1{\cdot}0271:1:1{\cdot}7663$, and $\beta=93° 42'$ for $(NH_4)_2Cr_2O_7$. Although the monoclinic crystals of the dichromate are the unstable form, they exhibit false equilibrium, and can be kept in contact with triclinic crystals in the cold without any appreciable change. They dissolve in a soln. saturated with respect to triclinic crystals at 12·5°, whereas triclinic crystals are unaffected under the same conditions. On heating, the monoclinic crystals decrepitate, and then behave like the triclinic crystals. The following description of potassium dichromate refers to the stable, triclinic forms unless stated otherwise. A. Duffour, and A. F. Hallimond discussed the isodimorphism of potassium and ammonium dichromates; H. E. Buckley, the effect of dichromates on the crystallization of sodium chlorate.

C. J. B. Karsten gave 2·603 for the sp. gr. of potassium dichromate; J. Schabus, 2·689; L. Playfair and J. P. Joule, 2·692 at 3·9°; and H. Schiff, 2·721. H. G. F. Schröder gave 2·702 for that which had been melted, 2·751 for that which had been melted and disintegrated, and 2·702 for the powdered salt. P. Kremers, and G. T. Gerlach gave for the sp. gr. of soln. at 19·5°/19·5°:

$K_2Cr_2O_7$.	1	3	5	7	9	11	13	15 per cent.
Sp. gr. .	1·867	1·022	1·037	1·050	1·065	1·080	1·097	1·110

F. Flöttmann gave for the sp. gr. at 15°, 20°, and 25°, respectively, 1·0635, 1·0768, and 1·0916. For A. Heydweiller's observations, *vide infra*. J. A. Ewing and J. G. MacGregor gave for soln. with 0·99, 2·44, 4·76, and 7·69 per cent. $K_2Cr_2O_7$ the respective values 1·0069, 1·0172, 1·0345, and 1·0561 at 10°/4°; and F. Fouqué gave for soln. with 5·9 grms. of $K_2Cr_2O_7$ per 1000 grms. of water 1·0045 at 0°/4°; 1·0037 at 16·4°/4°; 1·9812 at 75·5°/4°; and 1·9651 at 99°/4°; for soln. with 37·3 grms. of salt per 1000 grms. of water, 1·0257 at 0°; 1·0234 at 19·6°; 1·0030 at 69·6°; and 0·9843 at 99°; and for soln. with 89·2 grms. of salt per 1000 grms. of water, 1·0635 at 16°; 1·0349 at 79°; and 1·0221 at 99·5°. Observations on the sp. gr. were also made by E. F. Anthon, R. L. Datta and N. R. Dhar. R. Lorenz and W. Herz studied the critical density of this and related salts. J. N. Rakshit studied the contraction which occurs when potassium dichromate is dissolved in water, and in ethyl alcohol. K. F. Slotte found the sp. gr. of soln. of potassium dichromate with 4·71 and 6·97 per cent. $K_2Cr_2O_7$ to be respectively 1·0325 at 11°, and 1·0493 at 10·6°; and the viscosities (water 100) respectively 98·9, and 98·6 at 10°; 76·2 and 76·9 at 20°; 61·7 and 62 at 30°; and 51·1 and 51·4 at 40°. A. Kanitz gave for $2N$-, $4N$-, and $8N$-soln. the respective viscosities 1·0061, 1·0034, and 0·9999 (water unity) at 25°. L. J. Simon measured the viscosity of soln. of the salt—*vide supra*, potassium chromate. I. Traube gave 235·9 mgrms. for the drop-weight of the molten salt. R. Lorenz and W. Herz gave 123·6 for the surface tension at the b.p., and 140·6 at the m.p. R. Lorenz and H. T. Kalmus gave for the viscosity η in C.G.S. units:

	397°	417°	437°	457°	477°	497°	507°
η .	0·1339	0·1187	0·1059	0·0938	0·0823	0·0715	0·0664

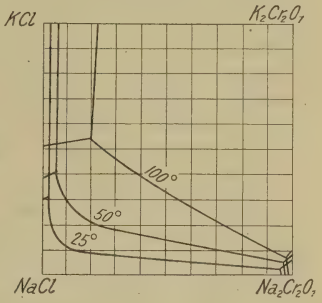


FIG. 70.—Reciprocal Salt Pair : $K_2Cr_2O_7+2NaCl=2KCl+Na_2Cr_2O_7$.

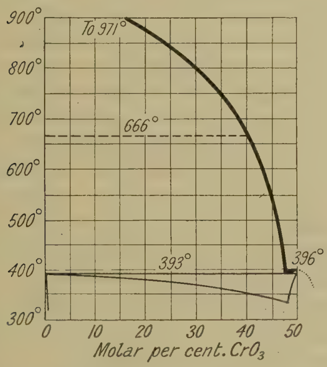


FIG. 71.—Freezing-point Curve of Mixtures of $K_2Cr_2O_7$–KCl.

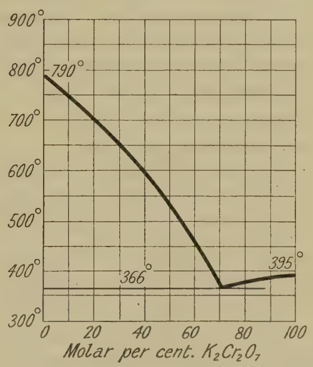


FIG. 72.—Freezing-point Curve of Mixtures of $KCrO_4$–CrO_3, or of $K_2Cr_2O_7$–K_2CrO_4.

F. Rüdorff found that the salt in aq. soln. diffuses through a membrane without dissociation. According to T. Sabalitschka and G. Kubisch, when soln. of potassium dichromate are dialyzed, the ratio K : Cr outside the dialyzer is not constant but is greater than 1. Chromic acid dialyzed more quickly than potassium chromate. Hence, it was inferred that potassium dichromate is partly decomposed into normal chromate and trichromate in dil. aq. soln. : $2K_2Cr_2O_7 \rightleftharpoons K_2CrO_4+K_2Cr_3O_{10}$. L. Playfair and J. P. Joule found the coeff. of thermal expansion—cubical—of the salt to be 0·0122 between 0° and 100°. F. E. Neumann gave 0·1857 for the sp. ht. ; while H. Kopp gave 0·186 between 21° and 52° ; H. V. Regnault, 0·186 between 16° and 98° ; and P. Nordmeyer and A. L. Bernoulli, 0·1386 between —186° and 20°. T. Thomson observed that the dichromate decrepitates when heated, and melts at a temp. much below redness, forming a transparent, red liquid, which on cooling solidifies to a red fibrous mass, which falls to pieces spontaneously—*vide supra.* C. Schubert, and W. Hempel and C. Schubert, observed that the evolution of gas sets in at 500°, and has not ceased as the temp. is raised to 1500° ; the reaction is represented $4K_2Cr_2O_7=3O_2+2(Cr_2O_3.2K_2CrO_4)$. A. Eucken and G. Kuhn gave 0·00395 to 0·00417 for the sp. ht. of large crystals at —190° ; and at 0°, 0·00428 to 0·00429. S. F. Schemtschuschny found that the stable form at the higher temp. has the m.p. 395° ; E. Groschuff gave 396° ; H. S. Roberts, 397·5° ; and P. L. Robinson and co-workers gave 398·4°±0·5°. S. F. Schemtschuschny found that the m.p. diagram of mixtures of potassium chloride and dichromate has two branches meeting at the eutectic 366° and 27·5° molar per cent. of the chloride—Fig. 71. Solid soln. are formed only on the dichromate side of the curve, these contain about 25 molar per cent. of chloride. Sections viewed under the microscope have the uniform structure of solid soln. only when taken from the dichromate side of the eutectic, those on the chloride side show crystals of chloride embedded in the groundwork of the eutectic mixture. J. B. Robertson studied the equilibrium diagram for the system $Na_2Cr_2O_7+2KCl \rightleftharpoons K_2Cr_2O_7+2NaCl$ at 25°, 50°, and 100° ; the results are plotted in Fig. 70. Potassium dichromate and sodium chloride are the compatible salt pair at all temp. ; as the temp. increases the areas on the diagram representing potassium and sodium chlorides increase considerably at the expense of the area representing potassium dichromate. The sodium dichromate area is always very small. E. Groschuff found that the f.p. curve of mixtures of potassium chromate and dichromate falls regularly from the m.p. of the chromate at 971° to the eutectic at 393° and 99 per cent. of dichromate, and it then rises to 396° the m.p. of the dichromate. At the transition temp., $\alpha\text{-}K_2CrO_4 \rightleftharpoons \beta\text{-}K_2CrO_4$, 666°, the mixture contains about 75·5 per cent. of dichromate—Fig. 72. E. Groschuff's attempts to obtain the f.p. curve of mixtures of potassium chromate with over 50 molar per cent. of chromic acid were not successful owing to the decomposition of the chromic acid—Fig. 72. Potassium dichromate suffers considerable decomposition when heated to the m.p. of the monochromate. P. Grouvelle observed that at a high temp. potassium dichromate decomposes into potassium chromate, chromic oxide, and oxygen.

M. Amadori studied the m.p. of mixtures of potassium dichromate with the dimolybdate and the ditungstate. The f.p. of $0{\cdot}5M$- and $0{\cdot}1M\text{-}K_2Cr_2O_7$ is found by R. Abegg and A. T. Cox to be respectively —0·27° and —0·49°; I. Koppel and E. Blumenthal gave —0·63° for the f.p. of a sat. soln. having 4·5 grms. of salt per 100 grms. of water. This is the cryohydric or eutectic temp. for which F. Guthrie gave —0·7° with $0{\cdot}18M$-soln., and C. M. Guldberg, —0·8° with $0{\cdot}15M$-soln. M. S. Sherrill found the lowering of the f.p. of very dil. soln., and calculated the ionization factor i—**1**. 10, 15—to be:

$K_2Cr_2O_7$	$0{\cdot}0005M$-	$0{\cdot}001M$-	$0{\cdot}00510M$-	$0{\cdot}1234M$-	$0{\cdot}02053M$-
F.p. .	—0·00362°	—0·00706°	—0·0350°	—0·070°	—0·113°
i .	3·9	3·8	3·70	3·07	2·98

$K_2Cr_2O_7$.	$0{\cdot}03004M$-	$0{\cdot}05340M$-
F.p. . .	—0·158°	0·263°
i . .	2·84	2·66

The first two sets of determinations quoted are by T. G. Bedford. The fact that the factor i in dil. soln. approaches to 4 means that not only is the molecule $K_2Cr_2O_7$ ionized into three ions $K_2Cr_2O_7 \rightleftharpoons 2K^{\cdot} + Cr_2O_7''$, but that the acid residue is also hydrolyzed: $Cr_2O_7'' + H_2O \rightleftharpoons 2HCrO_4'$. H. G. Leopold and J. Johnston found the mol. lowering of the vap. press. of soln. containing 0·4, 0·6, and $1{\cdot}0M\text{-}K_2Cr_2O_7$ to be respectively 0·0498, 0·0472, and 0·0419. P. Kremers gave 104° for the b.p. of a sat. soln.; M. Alluard gave 103·4° at 718 mm. press.; and I. Koppel and E. Blumenthal, 104·8° for a soln. with 108 grms. of salt per 100 grms. of water. A. Speransky found that the vap. press., p mm., of sat. soln. of the dichromate between 30·06° and 54·75° can be represented by $p=K\{(\theta—77{\cdot}407)/\theta\}^{50}$, where $\log K=7{\cdot}89408$. R. Lorenz and W. Herz studied some relations between the b.p. and the critical temp. W. Herz gave 29·8 Cals. for the heat of fusion per gram. J. G. F. Druce discussed the creeping of the salt during evaporation. M. Berthelot gave for the heat of formation, $(2H_2CrO_{4aq.}, 2KOH_{aq.})$=27·2 Cals. at 8°; 26·8 Cals. at 12°; 26·4 Cals. at 18°; P. Sabatier gave 27·0 Cals. at 17°; and F. Morges, 24·982 Cals. at 19·5°. M. Berthelot also gave $(2CrO_{3aq.}, 2KOH_{aq.})$=43·8 Cals. at 12°; and $(2CrO_{3solid}, 2KOH_{solid})$=106·8 Cals. at 12°; $(2Cr(OH)_3, 2KOH_{aq.}, 3O) = K_2Cr_2O_{7aq.}$+37·8 Cals. at 8°, and with $K_2Cr_2O_{7solid}$, 54·8 Cals. at 8°; and with KOH_{solid} and $K_2Cr_2O_{7solid}$, 113·0 Cals. at 8°; $(K_2CrO_{4solid}, CrO_{3solid})$=15·0 Cals., and $K_2Cr_2O_7$(12 litres of water)+4KOH(8 litres of water)=$2K_2CrO_{4aq.}$+23·6 Cals. at 12°; while P. Sabatier gave 23·0 Cals. at 17°. H. Rose said that the dichromate dissolves in water with a feeble absorption of heat. For the heat of soln., T. Graham gave —17·08 Cals.; F. Morges gave for a mol of the salt in 825 mols of water —17·169 Cals. at 19·5°; J. Thomsen, with 400 mols. of water, —16·7 Cals. at 18°; and with 653·5 mols of water, M. Berthelot gave —17·02 Cals. at 11·6°, or —17·02–6(θ—15) Cals. at θ°. E. von Stackelberg gave for a mol of $K_2Cr_2O_7$ at 17·5° with n mols of water:

n . . .	∞		1000		500		250		167
Heat of solution	18,400		17,440		16,885		16,335		16,000 cals.
Heat of dilution		960		555		550		335	

H. Dufet gave for the indices of refraction of the triclinic crystals α=1·7202, β=1·7380, and λ=1·8197 for the Na-line; and β=1·7209 for the Li-line; and P. L. Stedehouder and P. Terpstra gave for the pleochroic monoclinic crystals α=1·715, β=1·762, and γ=1·892. F. Fouqué found for the refractive indices, μ, with the D-line with soln. of 5·9 grms. of $K_2Cr_2O_7$ in 1000 grms. of water:

	9·0°	17·8°	50·0°	60·0°	70·0°	80·0°	93·2°
μ . .	1·3357	1·3350	1·3305	1·3289	1·3269	1·3259	1·3216

with soln. of 37·3 grms. $K_2Cr_2O_7$ per 1000 grms. of water:

	6·8°	16·0°	50·0°	60·0°	70·0°	80·0°	92·5°
μ . .	1·3413	1·3405	1·3340	1·3340	1·3322	1·3300	1·3270

and with soln. of 89·2 grms. of $K_2Cr_2O_7$ per 1000 grms. of water:

	16·8°	40·0°	50·0°	60·0°	70·0°	80·0°	95·4°
μ . .	1·3508	1·3476	1·3459	1·3441	1·3420	1·3397	1·3360

F. Flöttmann gave for soln. sat. at 15°, 20°, and 25° the values 1·35028, 1·35345, and 1·35685 for the D-line. J. Wagner, E. Viterbi and G. Krauz, A. Lallemand, E. Forster, K. Vierordt, P. Bary, B. K. Mukerji and co-workers, and R. L. Datta and N. R. Dhar made observations on this subject; and M. G. Mellon studied the colour of the soln. J. H. Gladstone gave for the equivalent refraction with the μ-formula, 79·9. The extinction coeff. of 0·03399M-$K_2Cr_2O_7$ for light of wave-lengths λ=508·6$\mu\mu$, 520·9$\mu\mu$, 536$\mu\mu$, and 546·1$\mu\mu$ are respectively 2·12, 0·976, 0·246, and 0·117. L. R. Ingersoll found Verdet's constant for the **electromagnetic rotatary power** for light of wave-length 0·6, 0·8, 1·0, and 1·25μ to be 0·0108, 0·0064, 0·0042, and 0·0025 respectively for soln. of sp. gr. 1·085. The **absorption spectrum** was studied by P. Sabatier, A. Étard, O. Knoblauch, F. Grünbaum, K. S. Gibson, H. C. Jones and W. W. Strong, T. Aden, N. R. Tawde and G. R. Paranjpe, G. Jander, J. Formanek, W. Böhlendorff, H. Bremer, F. Melde, G. Rössler, J. Müller, J. M. Hiebendaal, H. Settegast, and C. P. Smyth. I. Plotnikoff and M. Karsulin observed that the absorption of light by potassium dichromate begins at 595$\mu\mu$, and extends towards the ultra-violet. The photochemical absorption begins at 595$\mu\mu$ in the yellow, reaches a maximum at 500$\mu\mu$ in the green, and then decreases to about 240$\mu\mu$. According to C. Schaefer and M. Schubert, the ultra-red reflection spectrum of potassium dichromate has three maxima, one at 18·12μ, and complex ones at 12·14μ to 13·22μ, and at 10·44μ to 11·1μ. A. E. Lindh, D. Coster, and O. Stelling studied the **X-ray spectra**. H. von Halban and K. Siedentopf, and J. B. Ferguson discussed the potassium dichromate and molybdenum nitrate light filter. H. M. Vernon estimated the degree of ionization of aq. soln. of the salt from the colour. I. Plotnikoff, and M. Schwarz studied the photochemical oxidation of organic compounds by dichromates and chromates—*vide supra*, chromium trioxide. A. Reychler observed that in darkness there is no perceptible action between potassium iodide, and dichromate, and eosin in aq. soln., but in light iodine is liberated. A. Kailan found that an aq. soln. of potassium dichromate is reduced at the rate of 3×10^{11} mol per second by exposure to radium rays. R. Hunt thought that actinized soln. of potassium dichromate produce precipitates of chromates of a different colour from those obtained from soln. made and kept in the dark. F. Bush showed that the difference is due to the difference in the rate of mixing the soln., and not an effect of actinization—*vide supra*, silver chromate. T. Svensson studied the change in the conductivity, and potential of soln. of potassium dichromate in sulphuric acid when exposed to light. W. Herz gave $2{\cdot}42\times10^{12}$ for the vibration frequency. A. Kailan found that the salt is decomposed by exposure to radium radiations. E. Montignie observed that potassium dichromate, after exposure to ultra-violet light, affects a photographic plate.

J. A. Fleming and J. Dewar found that the dielectric constant of water with some potassium dichromate in soln. is not much affected, and similarly at −185°.

W. Schneider observed no piezoelectric effect. R. Lorenz and H. T. Kalmus found the sp. electrical conductivity of the fused salt to be:

	397°	417°	437°	457°	477°	497°	507°
Sp. cond.	0·1959	0·2381	0·2745	0·3109	0·3473	0·3837	0·4019 mho.

Observations on the conductivity of aq. soln. were made by R. Lenz, M. S. Sherrill, P. Walden, and J. Lundberg. A. Heydweiller found for 0·1*N*-, 0·2*N*-, and 0·5*N*-soln., the respective values 0·01010, 0·02012, and 0·05005 for the sp. gr. at 18°, and 98·2, 93·1, and 85·4 for the eq. electrical conductivities. H. C. Jones and C. A. Jacobson observed the mol. conductivity, μ mho, between 0° and 35°, and A. P. West and H. C. Jones between 35° and 65° when a mol of the salt is dissolved in v litres:

v		8	16	32	128	512	1024	2048
μ	0°	116·3	128·7	137·5	152·6	190·6	204·9	214·6
	10°	153·7	171·1	184·2	204·5	260·8	280·5	294·3
	25°	216·9	243·0	262·9	297·0	384·0	420·5	441·7
	35°	261·7	294·5	319·9	365·3	475·4	522·8	553·4
	65°	352·9	—	396·9	417·9	426·8	—	448·9
α	0°	54·2	60·0	64·1	71·1	88·8	95·5	100·0
	35°	47·3	53·2	57·8	66·0	85·9	94·5	100·0
	65°	78·6	—	88·4	93·1	95·1	—	100·0

The calculated values for the percentage ionization, α, are also indicated. W. C. D. Whetham gave for the eq. conductivity, λ mho, with soln. containing *N*-gram-equivalents per litre at 0°:

N	0·00001	0·0001	0·001	0·01	0·1	0·2
λ	81·3	76·3	71·4	70·4	64·3	61·5

and inferred from the small rise in conductivity with increasing dilution soln. of medium conc., and a larger change with soln. of small conc., that in the former case the ionization proceeds $Cr_2O_7'' + H_2O \rightleftharpoons 2HCrO_4'$, and in the latter case $HCrO_4' \rightleftharpoons H^{\cdot} + CrO_4''$. E. Spitalsky found the $H^{\cdot}$-ion conc., from observations on the effect of the dichromate soln. on the velocity of hydrolysis of diazoacetic ether, to be 0·000259 with soln. containing 0·1012 mol of $K_2Cr_2O_7$ per litre, and 0·000188 with soln. containing 0·0664 mol per litre. W. V. Bhagwat and N. R. Dhar found that the salt exists in aq. soln. probably as $KHCr_2O_4$. G. P. Vincent studied the depolarizing action of acidic soln. of the dichromate on hydrogen liberated at a smooth platinum electrode. T. Murayasu studied the conductivity of soln. in glycine. W. Spring observed that soln. of dichromate, on standing, slowly change their colour, and their electrical conductivity; this means that there is a slow change in the condition of the soln.—*vide supra*, potassium chromate, and chromic acid. H. Buff observed that on electrolysis of the molten salt, oxygen is evolved at the anode; and F. Morges added that the dichromate is reduced to chromate at the cathode—*vide supra*. For the photochemical action of light, *vide* chromic acid. S. Schlivitch observed a photovoltaic effect with soln. of potassium dichromate and platinum electrodes. F. Weigert studied the electrolytic reduction of soln. of the dichromate. J. B. Johnson discussed the e.m.f. due to the thermal agitation of a soln. of the dichromate.

G. Meslin said that potassium dichromate is paramagnetic. He found that the magnetic susceptibility of the powder is $0·13\times10^{-6}$ mass unit; and G. Quincke gave for a soln. of the dichromate between 18° and 20°, $0·76\times10^{-6}$ mass unit. J. Forrest measured the variations in the parallel and transverse components of the magnetization of the crystals. P. Weiss and P. Collet found the paramagnetism of a soln. of the dichromate is constant between 14° and 50°; and the subject was discussed by P. Weiss, L. A. Welo and A. Baudisch, and S. Berkman and H. Zocher. W. G. Hankel and H. Lindenberg found that the crystals exhibit pyroelectricity in that when warmed the (001)-face is usually positively electrified, and the (00$\bar{1}$)-face negatively electrified—the reverse behaviour is rare.

T. Thomson said that potassium dichromate has a cooling, bitter, metallic taste ; it is stable in air, and is not hygroscopic. V. Ipatieff and A. Kisseleff found that when $2N$-$K_2Cr_2O_7$ with some conc. sulphuric acid is exposed to hydrogen at 180° to 200 atm. press., a crystalline compound, $K_2O.Cr_2O_3.Cr_2(SO_4)_3.H_2O$, is formed. It is insoluble in acid, and is dissolved by molten sodium carbonate and potassium nitrate. H. P. Cady and R. Taft found potassium dichromate to be appreciably soluble in phosphoryl chloride, and very slightly soluble in liquid sulphur dioxide. According to C. F. Cross, in an atm. sat. with moisture, a mol of the salt takes up 3·5 mols of water which is removed by pressing it between filter-papers. Observations on the solubility of potassium dichromate in water were made by T. Thomson, H. Moser, M. le Blanc, M. Alluard, P. Kremers, M. S. Sherrill, A. Michel and L. Krafft, and H. G. Greenish and F. A. U. Smith. The following observations on the percentage solubility, S, are due to I. Koppel and E. Blumenthal for temp. below 100°, and to W. A. Tilden and W. A. Shenstone for temp. above 110° :

	−0·63°	0°	30°	60°	104·8°	117°	148°	180°
S . .	4·31	4·43	15·40	31·30	52·00	56·10	66·80	72·50

—*vide* Figs. 36 to 41. F. A. H. Schreinemakers gave 18·12 per cent. at 30°. A. Étard obtained the following values for S :

	1°	20°	61°	104°	150°	215°	312°	360°
S . .	4·1	10·4	30·2	48	60·8	76·9	91·8	97·4

but the results are considered to be too low. F. Flöttmann found the solubility at 15°, 20°, and 25° to be 0·321, 0·396, and 0·482 mols per litre, or 8·893, 10·822, and 12·980 per cent. R. Marc, M. le Blanc and W. Schmandt, and E. V. Murphree measured the rate of soln. of the salt in water, and showed that the process is determined by the rate of diffusion of the salt from the surface of the solid into the body of the liquid. J. Traube and W. von Behren discussed the formation of submicrons during the dissolution of the dichromate. T. Thomson said that an aq. soln. of the salt reddens litmus, and R. T. Thomson, and J. A. Wilson, that it is neutral towards lacmoid. The hydrolysis, $Cr_2O_7'' + H_2O \rightleftharpoons 2CrO_4'' + 2H^{\cdot}$, was studied by J. Sand and K. Kästle, and the equilibrium constant, $K = [CrO_4'']^2[H^{\cdot}]^2/[Cr_2O_7'']$, could not be determined satisfactorily owing to unrecognized disturbing conditions, but approximate estimates gave $K = 1{\cdot}5 \times 10^{-13}$ at 25° ; consequently, a $0{\cdot}1N$-soln. is 0·18 per cent. hydrolyzed. W. Herz and F. Hiebenthal gave for the solubility of potassium dichromate, S, one-sixth mol per litre, in n-normal soln. of lithium chloride, etc. :

LiCl	n . .	0	0·49	0·92	1·78	2·78	3·61	4·49
	S . .	2·89	2·78	2·55	2·26	1·85	1·37	1·32
NaCl	n . .	0·47	0·94	1·91	2·84	3·80	4·21	5·63
	S . .	2·91	2·98	2·79	2·62	2·33	2·24	2·06
NH_4Cl	n . .	0·73	1·79	2·59	3·10	4·00	5·32	
	S . .	2·82	2·54	2·32	2·16	1·83	0·91	
$MgCl_2$	n . .	0·45	0·93	1·84	2·31	2·74	3·15	
	S . .	2·78	2·64	2·24	2·07	1·91	1·76	
$CaCl_2$	n . .	0·24	0·45	0·92	1·41	1·64	1·87	11·42
	S . .	2·88	2·91	2·84	2·69	2·62	2·56	1·88
$SrCl_2$	n . .	0·51	1·00	2·02	2·28	2·84	3·47	
	S . .	2·89	2·91	2·73	2·69	2·62	2·38	

where for LiCl, $S = 2{\cdot}90 - 0{\cdot}352n$; for NaCl, $S = 3{\cdot}195 - 0\text{-}230n$; for NH_4Cl, $S = 3{\cdot}066 - 0{\cdot}309n$; for $MgCl_2$, $S = 2{\cdot}95 - 0{\cdot}380n$; for $CaCl_2$, $S = 3{\cdot}02 - 0{\cdot}250n$; and for $SrCl_2$, $S = 3{\cdot}12 - 0{\cdot}210n$.

A. C. Robertson represented the catalytic action of the dichromate on hydrogen dioxide by the cyclic reactions : $K_2Cr_2O_7 + H_2O_2 = 2KCrO_4 + H_2O$, and $2KCrO_4 + H_2O_2 = K_2Cr_2O_7 + H_2O + O_2$. E. Pietsch and co-workers studied the surface-conditions in the reaction between potassium dichromate and hydrogen dioxide. For the action of hydrogen dioxide, *vide infra*, perchromates. J. W. Thomas found that potassium dichromate first forms potassium chloride, and chromium trioxide, and then a brown chromium oxide, but no chromyl chloride.

W. K. van Haagen and E. F. Smith found that hydrogen fluoride passed over heated potassium dichromate removes nearly all the chromium. According to F. Fichter and E. Brunner, if a dil. soln. of potassium dichromate is treated with fluorine, it becomes green and is reduced to a chromic salt, most probably the fluoride. Crude fluorine always containing free hydrogen fluoride; the action of fluorine upon an aq. soln. furnishes hydrofluoric acid and its conc. may be sufficient for the formation of chromic fluoride. In this case, fluorine acts as a reducing agent. This contradictory behaviour must be explained by the intermediate formation of hydrogen dioxide, thus: $2H_2O+F_2=H_2O_2+2HF$. The formation of hydrogen dioxide can be detected by working with a small quantity of chromic acid and in the presence of dil. sulphuric acid; under these conditions and by proper cooling we obtain the blue perchromic acid, soluble in ether. Perchromic acid is very unstable, losing oxygen and yielding chromic salts; in this manner the reduction of dichromate can be carried out quantitatively by prolonged treatment with fluorine. K. H. Butler and D. McIntosh observed that the dichromate is insoluble in liquid chlorine, and has no action on the b.p. of the liquid. According to E. M. Péligot, a soln. of potassium dichromate in boiling hydrochloric acid deposits, on cooling, potassium chlorochromate. R. E de Lury, and G. Kernot and F. Pietrofesa concluded from their observations on the action of potassium dichromate on acidic soln. of iodides that the reaction is of the first order with respect to the Cr_2O_7''-ion, nearly of the second order with respect to the $H^{\cdot}$-ion, and between the first and second order with respect to the I'-ion. R. F. Beard and N. W. Taylor showed that there are many anomalous results in connection with the reaction: $Cr_2O_7''+6I'+14H^{\cdot}=2Cr^{\cdots}+7H_2O+3I_2$, which disappear in the presence of $1{\cdot}5M$-NaCl. Two simultaneous reactions occur: $H^{\cdot}+I'+Cr_2O_7''\rightarrow HI.Cr_2O_7''$; and $2H^{\cdot}+2I'+Cr_2O_7''\rightarrow(HI)_2.Cr_2O_7''$. The velocity constant, k, is given by $k=14{\cdot}6[H^{\cdot}][I']+53000[H^{\cdot}]^2[I']^2$. The reaction was studied by N. A. Izgarischeff and A. K. Belaieff.

J. B. Senderens found that a soln. of potassium dichromate is decolorized by boiling it with sulphur, forming Cr_7O_{12}, or $3Cr_2O_3.CrO_3$, and a soln. of potassium sulphate and thiosulphate. A. Manuelli found that if a mixture of sulphur and the dichromate is heated in a sealed tube, chromic oxide is formed; and K. Brückner said that the reaction of the dichromate resembles that of the monochromate (*q.v.*) with sulphur—*vide supra*, the preparation of chromic oxide. A. A. Hayes said that hydrogen sulphide precipitates some hydrated chromic oxide mixed with sulphur; and P. Berthier, that sulphur dioxide colours the soln. green forming potassium chromic sulphate and dithionate. H. Bassett said that 94–95 per cent. of chromic sulphate and 5–6 per cent. of dithionate are formed. W. R. Hodgkinson and J. Young studied the action of dry sulphur dioxide on the salt. O. Popp represented the reaction with sodium thiosulphate: $2K_2Cr_2O_7+Na_2S_2O_3=K_2CrO_4+Cr_2O_3.CrO_3+K_2SO_4+Na_2SO_3$. W. H. Balmain found that when 3 parts of the dichromate are heated with 4 parts of sulphuric acid, chromium and potassium sulphates, water, and oxygen are formed, and he used this mode of preparing oxygen in preference to the potassium chlorate process—*vide supra*, chromium trioxide. G. Grather and T. Nagahama observed that potassium dichromate is reduced by sodium sulphide, sulphite, and thiosulphate in the order of increasing effect. M. Traube found that a mol of the salt dissolved in 3·5 parts of water and treated with 2 mols of H_2SO_4 in the cold is not decomposed, but it is decomposed by 3 mols of sulphuric acid with 0·5 part of water per mol of salt, but not with 2 parts of water. H. Schwarz made observations on this subject—*vide supra*, the preparation of chromium trioxide. E. C. Franklin and C. A. Kraus found that the salt is insoluble in liquid ammonia. The action of ammonium chloride has been indicated in connection with the preparation of chromic oxide. F. Santi found that a conc. soln. of ammonium chloride may convert the dichromate to chromic acid. According to G. B. Frankforter and co-workers, the reaction which takes place when the mixture is heated at 290° is different from that which occurs at a dull red-heat, the composition of the gas evolved and of the residue left after lixiviation being different in the two cases. A mixture of ammonium chloride and potassium dichromate does not undergo any change until a temp. of 210° is attained. The mixture then becomes yellowish-brown, owing to the formation of chromium dioxide. At 260°, a slate-coloured residue is obtained, which, on lixiviation with water, leaves small, greenish-black, iridescent spangles of a hydrated chromium oxide, $Cr_2O_3.2H_2O$. The change which takes place does not depend only on the temp., but also on the proportions of the salts employed. At 370°, in presence of a considerable excess of ammonium chloride, chromium chloride and ammonia are formed. If, however, the potassium dichromate is in large excess, a black residue is obtained, together with some unchanged dichromate. Under certain conditions, chlorine is liberated, and in some cases, a nitride of chromium is produced. It is supposed that the complexity of the reaction is largely due to the dissociation of ammonium chloride, which is the first change to take place when the mixture is heated. E. Mitscherlich, and F. Bothe found that a soln. of the salt in nitric acid deposits crystals of the terchromate. E. Kopp said that phosphorus reduces the soln. in sunlight or when heated, forming potassium chromate and a little chromium phosphate. A. Michaelis found that in a sealed tube, the salt is partially decomposed phosphorus trichloride at 166°, forming potassium chlorochromate, phosphoryl chloride, potassium phosphate, and chromium chromate. A mixture with carbon detonates slightly when heated. S. Levites studied the adsorption of the salt from aq. soln. by charcoal. E. J. Bowen and C. W. Bunn studied the photochemical oxidation of alcohols by dichromates. H. B. Weiser and E. B. Middleton attributed the conversion of potassium dichromate into chromate, observed by N. Ishizaka, to the disturbance of the equilibrium: $Cr_2O_7'' + H_2O \rightleftharpoons 2H^{\cdot} + 2CrO_4'$, by the preferential adsorption of $H^{\cdot}$-ions by the alumina. W. Kuczynsky found that a 4 per cent. soln. of potassium dichromate electrolytically pitted the surface of aluminium at 220 volts. J. Morland, and A. Reinecke studied the action of ammonium thiocyanate. B. Reinitzer found that the dichromate is insoluble in alcohol. E. J. Bowen and E. T. Yarnold studied the photochemical oxidation of ethyl alcohol by the dichromate. L. Godefroy studied the joint action of alcohol and chlorine or iodine; and A. Commaille, the joint action of acids and ether. F. W. O. de Coninck observed that 100 grms. of a sat. soln. in glycol contain 6 grms. of potassium dichromate. A. Naumann found that the salt is insoluble in benzonitrile, and acetone; and W. Eidmann, insoluble in acetone and methylal. D. Lindo observed that a brown colour is produced with phenol, and E. A. Parnell studied the joint action of phenol and hydrogen dioxide. J. Piccard and F. de Montmollin observed that the oxidation of aniline by potassium dichromate is a reaction of the second order. A. Commaille found that tannin gives a brown precipitate. For the action on gelatin, *vide supra*, chromic acid. G. Grather and T. Nagahama studied the reduction of dichromates to basic chromates by lactic acid, tartaric acid, glucose, dextrose, tannin, glycerol, formaldehyde, thiosulphates, sulphites, and sulphides, and found that the relative activity of these substances decreases in the order given. Methyl alcohol did not reduce the salt. J. W. Williams and E. M. Drissen investigated the action of the salt on cysteine. E. H. Riesenfeld and O. Hecht studied the photochemical reaction with ethylene glycol; and J. Plotnikoff, and D. S. Morton, the photoxidation of organic compounds by the dichromate.

S. Kern represented the reaction with magnesium: $K_2Cr_2O_7 + Mg + 2H_2O = MgCr_2O_7 + 2KOH + H_2$; and E. Heyn and O. Bauer observed that a dil. soln. of the dichromate dissolves iron, but soln. of certain concentrations retard the rusting of iron. W. P. Jorissen and G. M. A. Kayser discussed the reaction with sulphur and aluminium, and sulphur and iron. According to F. Margueritte, dil. soln. of potassium dichromate become paler in colour when treated with potassium chloride, nitrate, or sulphur, with ammonium nitrate or sulphate, or with sodium carbonate or tetraborate. H. J. P. Venn and V. Edge noted that basic cupric chlorides are formed by the action of a dil. soln. of potassium dichromate on cuprous chloride. When the dichromate is mixed with silicon and heated in the electric arc, L. Kahlenberg and W. J. Trautmann found that it is readily reduced to a porous green slag. J. C. Witt, and M. Neidle and J. C. Witt, studied the action of potassium dichromate on stannous sulphate and stannous chloride. According to E. R. Bullock, the reaction between silver in gelatin and a soln. containing potassium dichromate and a bromide, slightly acidified with acetic acid, only occurs in presence of potassium ferricyanide or copper sulphate, which appear to act as catalysts. The action of the catalyst is attributed to the greater simplicity of the initial ionic reaction: $\mathrm{Fe(CN)_6{}'''+Ag=Ag^{\cdot}+Fe(CN)_6{}''''}$, or $\mathrm{Ag+Cu^{\cdot\cdot}=Ag^{\cdot}+Cu^{\cdot}}$, as compared with $\mathrm{3Ag+Cr^{\cdot\cdot\cdot\cdot\cdot\cdot}=3Ag^{\cdot}+Cr^{\cdot\cdot\cdot}}$, which involves four ions instead of two. The concentrated soln. of potassium dichromate in $0\cdot3N$-NaOH increases up to 6·5 per cent. when shaken with animal charcoal—negative adsorption; with more dil. soln., the conc. is diminished—positive adsorption. The negative adsorption is explained on the assumption that the conc. of the water on the surface of the particles of charcoal is increased. E. Brentel recommended potassium dichromate as a standard for acidimetry. R. G. van Name and F. Fenwick studied the electrometric titration of ferrous salts with potassium dichromate; K. Someya, the action of potassium dichromate on potassium ferrocyanide; and M. M. Narkevich, the acceleration due to oxidation produced by the dichromate when copper dissolves in sulphuric acid.

W. K. Sullivan added that if an almost boiling soln. of a mol of potassium dichromate is treated with 2 mols of sulphuric acid, the orange-red crystals which separate on cooling appear to be *potassium dihydrosulphatodichromate* because they have the composition $\mathrm{K_2Cr_2O_7.2KHSO_4}$, but there is really nothing to show that this is a chemical individual. According to J. Fritzsche, *potassium disulphodichromate*, $\mathrm{K_2(Cr,S)_2O_7}$, or $\mathrm{KO.SO_2.O.CrO_2.OK}$, is formed in the preparation of chromic acid by the action of sulphuric acid on an excess of potassium dichromate. H. Reinsch, and H. Schiff, however, regarded the product so obtained as a mixture of potassium sulphate and dichromate. H. Schiff represented the action of fused potassium chlorochromate on potassium sulphate by the equation: $\mathrm{K_2SO_4+KCrO_3Cl=KCl+KO.CrO_2.O.SO_2.OK}$; and on potassium hydrosulphate, by: $\mathrm{KHSO_4+KCrO_3Cl=HCl+KO.CrO_2.O.SO_2.OK}$. He said that the colour of the salt is the same as that of potassium dichromate; and that it is decomposed by water into potassium sulphate and dichromate, and sulphuric acid.

L. Grandeau [5] prepared crystals of **rubidium dichromate**, $\mathrm{Rb_2Cr_2O_7}$, from a soln. of rubidium carbonate in an excess of a warm aq. soln. of chromic acid. F. A. H. Schreinemakers and A. Filippo's observations on the equilibrium conditions are summarized in Fig. 46. According to G. N. Wyrouboff, there are three forms, a monoclinic form and two triclinic forms, but observations by J. A. le Bel, W. Stortenbecker, and B. Gossner have established the existence of only two varieties—monoclinic and triclinic. W. Stortenbecker said that the monoclinic form is alone produced when soln. are crystallized below 35°, and the triclinic form when crystallization occurs at temp. above 75°; and J. A. le Bel said that the red triclinic variety alone crystallizes from acidic soln., whilst in the presence of a little alkali, the yellow monoclinic modification separates. The dimorphism is not conditioned by temp. alone. W. Stortenbecker added that the monoclinic and triclinic modifications of rubidium dichromate are monotropic, but that the small difference in stability between them retards the transformation of one into the other. If the time is great, the triclinic form is obtained, but a rapid crystallization gives sometimes the monoclinic, sometimes the triclinic, and sometimes a mixture of the two. This is probably the explanation of G. N. Wyrouboff's statement to the effect that, if crystals of one form are placed in contact with a sat. soln. of the other, they remain indefinitely without showing the slightest indication of transformation, no matter what the temp. G. N. Wyrouboff gave for the axial ratios of the monoclinic crystals $a:b:c=0\cdot596:1:0\cdot3388$, and $\beta=87°\ 8'$; while B. Gossner gave $1\cdot0202:1:1\cdot8081$, and $\beta=93°\ 28\cdot5'$. G. N. Wyrouboff found that the (010)-cleavage is incomplete, that the optic axial angle $2V=83°\ 16'$; the optical character is negative; and the sp. gr. is 3·021.

The axial ratios of the triclinic pinacoids are $a : b : c = 0{\cdot}5609 : 1 : 0{\cdot}5690$, and $\alpha = 91°\ 0'$, $\beta = 93°\ 52'$, and $\gamma = 81°\ 34'$. B. Gossner said that the (001)- and (010)-cleavages are complete, and that the (100)-cleavage is distinct. G. N. Wyrouboff found that the optical axial angle $2E = 107°\ 42'$; the optical character is positive; and the sp. gr. is 3·125. A. F. Hallimond discussed the mol. vols. of the isomorphous dichromates. The monoclinic form is considered by W. Stortenbecker to be the labile form more easily soluble in water; and he gave for the solubility, S per cent.:

		(14°)	18°	(26°)	30°	40°	(43°)	50°	65°
S	monoclinic	4·45	5·42	8·00	9·08	13·22	16·52	18·94	28·8
	triclinic	4·40	4·96	7·91	8·70	12·90	14·57	18·77	27·3

The data for the bracketed temp. were determined by G. N. Wyrouboff. According to J. A. le Bel, a red crystal placed in a soln. from which yellow crystals are separating passes into soln. so that the solubility of the two forms is not the same. F. A. H. Schreinemakers and A. Fillippo found that a sat. soln. contains 9·47 per cent. $Rb_2Cr_2O_7$ at 30°.

According to C. Chabrié,[6] the evaporation of an aq. soln. of 100 parts of cæsium chromate and 26 parts of chromium trioxide furnishes **cæsium dichromate,** $Cs_2Cr_2O_7$; F. R. Fraprie obtained the salt by treating cæsium chromate with sulphuric acid. The conditions of equilibrium worked out by F. A. H. Schreinemakers and D. J. Meijeringh are summarized in Fig. 47. C. Chabrié said that the pale red crystals are very stable; and F. R. Fraprie added that the crystals are triclinic with complete basal cleavage; and they are much more soluble in hot than in cold water. A. F. Hallimond discussed the mol. vols. of the isomorphous dichromates. F. A. H. Schreinemakers and D. J. Meijerinck represented for the solubilities of the different alkali dichromates, at 30°,

	Li	Na	NH_4	K	Rb	Cs
$M_2Cr_2O_7$	56·6	66·4	32·05	15·34	9·47	5·20

F. Dröge,[7] J. Schulze, and M. Gröger prepared **cupric dichromate,** $CuCr_2O_7.2H_2O$, by evaporating a soln. of cupric hydroxide in aq. chromic acid, and, if any green crystals separate, pouring off the clear soln., and evaporating the remaining liquor over conc. sulphuric acid. C. Freese obtained a basic chromate by this process. L. Balbiano obtained cupric dichromate by evaporating a soln. of the basic chromate in aq. chromic acid—if alcohol is added to the soln., a basic chromate is precipitated. A. Viefhaus obtained cupric dichromate from the soln. obtained by treating barium chromate with cupric sulphate, and J. Schulze, from the soln. of cupric carbonate in aq. chromic acid. F. Zambonini said that the triclinic crystals have the axial ratios $a : b : c = 0{\cdot}6133 : 1 : 0{\cdot}5117$, and $\alpha = 67°\ 2'\ 16''$, $\beta = 125°\ 14'\ 3''$, and $\gamma = 111°\ 26'\ 2''$; and the sp. gr. is 2·286 at 19°. F. Dröge, and J. Schulze said that the crystals of the dichromate are brownish-black; they lose all their water at 100°, and decompose at a red-heat; they deliquesce in air; are sparingly soluble in water without decomposition; they are also soluble in alcohol, and in aq. ammonia. N. Parravano and A. Pasta obtained cupric tetramminodichromate, $CuCr_2O_7.4NH_3.2H_2O$, in black prismatic crystals by evaporating an ammoniacal soln. of the compound which cupric dichromate forms with pyridine. J. Schulze said that if a soln. of cupric dichromate be treated with an excess of cupric carbonate, the basic product has a variable composition. A. and L. Lumière and A. Seyewetz observed that light reduces cupric dichromate gelatine less readily than gelatine with ammonium dichromate. N. Parravano and A. Pasta obtained complex salts with pyridine, aniline, and ethylenediamine. G. Krüss and O. Unger prepared **ammonium cupric dichromate,** $3(NH_4)_2Cr_2O_7.2CuCr_2O_7.6H_2O$, in dark brown tetragonal crystals, by evaporating or cooling a hot conc. soln. of 2 molar parts of ammonium dichromate and cupric dichromate. It loses its water, with some decomposition, at 100°; and at a higher temp., it decomposes with incandescence. The salt is soluble in water. A. Stanley reported **sodium copper dioxydichromate,**

$Na_2Cr_2O_7.2CuO.CuCr_2O_7.4H_2O$, by the action of a soln. of sodium dichromate on freshly-precipitated cupric hydroxide. The brown, microcrystalline powder loses water at 200°, and decomposes at a higher temp. It is almost insoluble in water; and only slightly soluble in alcohol.

According to H. Moser,[8] the action of chromic acid on a soln. of silver nitrate furnishes ruby-red crystals of **silver dichromate,** $Ag_2Cr_2O_7$; L. N. Vauquelin obtained the same salt from a soln. of silver chromate and nitric acid. O. Mayer, and W. Autenrieth used similar processes. R. Warington, C. Freese, W. Autenrieth, and E. Jäger and G. Krüss obtained the salt by adding potassium dichromate to a soln. of silver nitrate. A. Janek, and M. S. Dunin and F. M. Shemyakin studied the formation of rhythmic rings of silver dichromate. G. P. Baxter and R. H. Jess mixed potassium dichromate or chromic acid and silver nitrate in nitric acid, and crystallized silver dichromate from $0 \cdot 16N$- to $3N$-HNO_3, and dried the product at 150°, and afterwards powdered the product and dried it at 200° in a current of dry air. E. R. Riegel and M. C. Reinhard, D. A. Audalian, E. S. Hedges, and E. S. Hedges and R. V. Henley studied the formation of rhythmic rings of silver dichromate in gelatine—*vide supra*, silver chromate. R. Warington, and A. Helmsauer found that a silver plate becomes covered with scarlet crystals of silver dichromate when it is immersed in a soln. of potassium chromate and dichromate and sulphuric acid—a little chromic oxide is formed. G. H. Zeller said that heat hastens the formation of the crystals. The crystals appear dark brown or dark grey or black in reflected light, and scarlet-red or carmine-red in transmitted light. J. Schabus said that the triclinic pinacoids have the axial ratios $a:b:c=1 \cdot 5320:1:1 \cdot 0546$. H. G. F. Schröder found the sp. gr. to be 4·669; while G. P. Baxter and R. H. Jess gave 4·770 at 25°/4°. R. Warington found the dichromate to be sparingly soluble in water forming a bright yellow soln. which reddens litmus, and yields crystals on evaporation. When boiled with water, it forms dark green chromate, and an acidic soln. which deposits the dichromate on cooling; W. Autenrieth represented the reaction $Ag_2Cr_2O_7+H_2O=Ag_2CrO_4+H_2CrO_4$. O. Mayer gave for the solubility $1 \cdot 9 \times 10^{-4}$ mol per litre at 15°; and M. S. Sherrill and D. E. Russ, $7 \cdot 3 \times 10^{-3}$ mol per litre at 25°. M. S. Sherrill and D. E. Russ said that water, and nitric acid below $0 \cdot 06N$-HNO_3, decompose the dichromate with the separation of chromate. They found for the solubility, S milliatoms per litre, at 25°:

		HNO_3 .	$0N$-	$0 \cdot 01N$-	$0 \cdot 02N$-	$0 \cdot 04N$-	$0 \cdot 06N$-	$0 \cdot 08N$-	$0 \cdot 10N$-
S	Cr .	.	32·20	25·06	20·21	13·59	11·10	11·10	0·624
	Ag .	.	5·390	6·131	7·148	9·529	11·10	11·10	—
Solid phase.			$\underbrace{Ag_2CrO_4+Ag_2Cr_2O_7}$				$\underbrace{Ag_2Cr_2O_7}$		

R. Warington said that the salt is freely soluble in nitric acid and in aq. ammonia. A. Helmsauer said that when heated to redness, silver, and chromic oxide are formed. F. B. Hofmann observed that the powdered dichromate collects at the boundary surface when shaken with a mixture of water and benzene, toluene, xylene, or chloroform. S. H. C. Briggs observed the formation of complex salts with pyridine, $Ag_2Cr_2O_7.4$(and 6)C_5H_5N; and G. Krüss, and S. Darby, complex salts—$Ag_2Cr_2O_7.1$(and 2)$HgCy_2$. R. G. van Name and R. S. Bothworth found that when silver sulphate and dichromate, the former greatly in excess (99 : 1), are crystallized at a temp. of 25° from an acidic soln. (standard soln. of sulphuric acid), there are obtained solid soln. of sulphate and dichromate, ranging in colour from pale yellow to scarlet, and with the same rhombic form as the pure sulphate. These crystals contain up to 4·1 molar per cent. of dichromate. When a greater proportion of dichromate is present in the acidic soln., crystals of the dichromate alone separate. J. W. Retgers could not prepare solid soln. of these two salts. P. Ray and J. Dasgupta studied complexes with hexamethylenetetramine.

L. N. Vauquelin[9] prepared **calcium dichromate,** $CaCr_2O_7.3H_2O$, from a soln. of calcium oxide in chromic acid; and J. F. Bahr, from a soln. of calcium chromate in chromic acid, and evaporating the liquor over conc. sulphuric acid, or in vacuo. F. Mylius and J. von Wrochem supposed that the salt is tetrahydrated, but they obtained the dichromate, in red, six-sided plates, from a sat. soln. at 18°, when 61 per cent. of $CaCr_2O_7$ is present. When freshly prepared, the crystals of the trihydrate are red, but when left on a porous tile in a desiccator, they become yellowish-brown. They lose water when heated; and at a higher temp. they melt to a reddish-brown liquid. K. S. Nargund and H. E. Watson observed that calcium dichromate gives off oxygen at 250° in vacuo, and decomposes at 500° into calcium chromate and chromic oxide. Calcium dichromate behaves on heating like a mixture of calcium chromate and chromium trioxide. L. Schulerud could not prepare this salt. A. Naumann said that the dichromate is soluble in acetone. J. F. Bahr, A. Dalzell, and K. Preis and B. Rayman prepared **strontium dichromate,** $SrCr_2O_7.3H_2O$, from a soln. of strontium chromate in chromic acid. The crystals are coloured like those of potassium ferricyanide. G. N. Wyrouboff gave for the axial ratios of the monoclinic, prismatic crystals $a:b:c = 0{\cdot}6023:1:0{\cdot}5460$, and $\beta = 92°\ 32'$. The salt loses its water of crystallization at 110°; and at 220° all the water is expelled; and at a higher temp. oxygen is given off. K. Preis and B. Rayman, and W. Autenrieth obtained **barium dichromate,** $BaCr_2O_7$, by the action of a soln. of chromic acid on freshly precipitated barium chromate; and O. Mayer, by boiling barium chromate with chromic and nitric acids, and by adding barium chloride to a hot conc. soln. of chromic acid and washing the product with acetic acid. The brownish-yellow, or brownish-red, monoclinic prisms are decomposed by cold water into chromic acid and barium monochromate. O. Mayer said that the dichromate is not attacked by boiling acetic acid. According to J. F. Bahr, and E. Zettnow, the *dihydrate,* $BaCr_2O_7.2H_2O$, is formed by evaporating a soln. of barium chromate in chromic acid, but neither L. Schulerud nor W. Autenrieth could verify this. K. Preis and B. Rayman said that the dihydrate is produced by evaporating the mother-liquor from the preparation of the anhydrous salt. J. F. Bahr described the crystals as stellate groups of yellowish-brown needles; K. Preis and B. Rayman, as rhombic, brownish-yellow plates; and E. Zettnow, as dark yellow, doubly refracting scales which lose all their water at 120°. J. F. Bahr said that the salt is nearly all decomposed by water; and that barium dichromate separates from conc., aq. soln.; and barium monochromate from dil. aq. soln. For the equilibrium between barium chromate and dichromate, *vide* chromic acid.

B. Reinitzer[10] prepared **magnesium dichromate,** $MgCr_2O_7$; and he found the salt to be soluble in water; and slightly soluble in alcohol. G. A. Barbieri and F. Lanzoni obtained complex salts of magnesium dichromate with hexamethylenetetramine by the action of a conc. soln. of that base with potassium dichromate on a conc. soln. of magnesium acetate or sulphate. By evaporating in vacuo a soln. of a mol of zinc carbonate in 2 mols of cold chromic acid, J. Schulze[11] obtained dark reddish-brown crystals of **zinc dichromate,** $ZnCr_2O_7.3H_2O$. The crystals are hygroscopic in air; and freely soluble in water, but are decomposed by boiling water. The salt was also prepared by M. Gröger. C. O. Weber obtained what he regarded as *potassium zinc chromatodichromate,* $K_2Cr_2O_7.ZnCrO_4$. G. Krüss and O. Unger obtained a complex with mercuric cyanide; N. Parravano and A. Pasta, and S. H. C. Briggs, a complex with pyridine; and S. H. C. Briggs, a complex with aniline. J. Schulze obtained **cadmium dichromate,** $CdCr_2O_7.H_2O$, by the method employed for the zinc salt. The dark orange-brown crystals are easily soluble in water, and are not decomposed by that agent. G. Krüss and O. Unger, and M. Gröger also prepared this salt. N. Parravano and A. Pasta obtained complex salts with ethylenediamine, pyridine, and aniline. G. Krüss prepared hygroscopic **potassium cadmium dichromate,** $K_2Cr_2O_7.CdCr_2O_7.2H_2O$, which is soluble in water.

J. A. Atanasiu[12] found that in the electrometric titration of soln. of mercurous nitrate and potassium chromate the curve shows a break corresponding with

mercurous dichromate, $Hg_2Cr_2O_7$. A. J. Cox showed that **mercuric dichromate,** $HgCr_2O_7$, is also stable at 25°, with soln. having more than 10·46 mols of chromic acid per litre—Figs. 50 and 51—and this salt is the solid phase with soln. having between about 10·5 and 11·5 mols of chromic acid per litre. The same salt was prepared by A. Gawalowsky by the action of potassium dichromate on a soln. of mercuric nitrate. The deep carmine-red crystals were found by S. H. C. Briggs to form complex salts with pyridine. They also form complexes with other mercuric salts—chloride, cyanide, etc. K. A. Hofmann recommended a soln. of mercuric chromate in chromic acid for oxidizing carbon monoxide in gas-analysis. C. Hensgen prepared **ammonium oxydimercuriammonium dichromate,** $3(NH_4)_2Cr_2O_7[NH_2(HgOHg)]_2Cr_2O_7$, by boiling a soln. of ammonium dichromate with mercuric oxide; or by saturating a hot, conc. soln. of ammonium dichromate with yellow mercuric oxide, and washing with water, alcohol, and ether, the product which separates on cooling. The yellow needles or plates do not decompose in air. The salt decomposes with detonation when heated rapidly, and when slowly heated to 170°–200°, it forms a black, graphitic mass which detonates suddenly at a higher temp. It is insoluble in water, alcohol, and ether. Three-fourths of the nitrogen is evolved as ammonia when the salt is heated with potash-lye, and oxydimercuriammonium chromate is formed. The same product is obtained by treating the salt with aq. ammonia. The salt is freely soluble in hydrochloric acid, and sparingly soluble in dil. nitric or dil. sulphuric acid; and it is decomposed by warm, conc. acids.

G. Calcagni[13] prepared **aluminium oxydichromate,** $Al_2O(Cr_2O_7)_2$, as an amorphous paste by evaporating a soln. of precipitated aluminium hydroxide in chromic acid. R. E. Meyer obtained a soln. of **indium dichromate** by dissolving the oxide in a warm soln. of chromic acid; but on evaporation in a desiccator, he was unable to crystallize the resulting syrupy liquid. W. Crookes,[14] and M. Hebberling obtained **thallous dichromate,** $Tl_2Cr_2O_7$, by adding potassium dichromate to a soln. of a thallous salt. L. Schulerud emphasized the need for using an acidified soln. of the thallous salt, otherwise a mixture of thallous chromate and dichromate is precipitated. J. E. Willm obtained the dichromate by boiling the chromate with dil. sulphuric acid; and E. Carstanjen, by dissolving thallous carbonate in an excess of chromic acid. The orange-yellow or orange-red, crystalline powder is insoluble in water. F. J. Faktor found that thallous dichromate is somewhat soluble in water; and with a soln. of sodium thiosulphate, it forms yellow chromate, Tl_2CrO_4. If the soln. of the dichromate in sodium sulphate is warmed with ammonium chloride, hydrated chromic oxide is precipitated.

O. Mayer[15] obtained **lead dichromate,** $PbCr_2O_7$, by treating a soln. of lead acetate with chromic acid in the presence of conc. nitric acid, sp. gr. 1·4; K. Preis and B. Rayman, by treating lead chromate with a conc. soln. of chromic acid—cold or hot; and E. Hatschek, by the action of ammonium chromate on a soln. of lead nitrate. E. Hatschek also studied the formation of the dichromate by allowing the ammonium dichromate to diffuse into an agar-agar soln. of lead nitrate; and V. Moravek, by the diffusion of lead nitrate into gels. of potassium dichromate. A. J. Cox studied the conditions of its formation from lead oxide and chromic acid—*vide* Fig. 55. It is formed when a mol of lead oxide is shaken with a sat. soln. of 2·5 mols of chromic acid at 25°. The excess of chromic acid is washed out with a more dil. soln. of chromic acid, and the product dried by press. between porous tiles, and then in a desiccator over calcium chloride. K. Elbs and R. Nübling prepared the dichromate by electrolyzing a 130 per cent. soln. of chromic acid between lead electrodes with an anode density of 4 to 3 amps. per sq. dm. at 15°–20°. They also obtained evidence of the formation of *plumbic dichromate,* $Pb(Cr_2O_7)_2$. The preparation of lead dichromate was also studied by J. Milbauer, who found that the dichromate is precipitated from soln. which are seven times molar with respect to CrO_3. The crystals cannot be washed by water without hydrolysis, but they can be freed from chromic acid by washing with a

10 per cent. soln. of glacial acetic acid in acetone. Electrolytic processes were studied by W. Borchers, and C. Lückow. K. Preis and B. Rayman obtained a *dihydrate*, $PbCr_2O_7.2H_2O$, but this has not been confirmed. Lead dichromate appears as a reddish-brown powder, or in brick-red needles, or as a crystalline powder. It is decomposed by water into lead chromate and chromic acid; it is stable in a soln. with at least 6·87 mols of CrO_3 per litre at 25°. It is soluble in soda-lye.

As indicated in connection with the basic bismuth chromates, there is a possibility that *bismuth hydroxychromate*, $Bi(OH)(CrO_4)$, is **bismuthyl dichromate,** $(BiO)_2Cr_2O_7.H_2O$; and that *bismuthyl quaterchromate*, $Bi_2O_3.4CrO_3.H_2O$, is **bismuthyl hydroxydichromate,** $Bi(OH)(Cr_2O_7)$. A. J. Cox[16] did not find bismuth dichromate on the equilibrium diagram, Fig. 63. K. Preis and B. Rayman prepared **potassium bismuthyl dichromate,** $K_2Cr_2O_7.(BiO)_2Cr_2O_7$, by mixing soln. of 2 mols of bismuth nitrate, and 3 mols of potassium chromate, and allowing the precipitate to stand in contact with the mother-liquor to crystallize. The pale or dark orange-red, granular or scaly powder is decomposed by water. It is soluble in hydrochloric acid. If this salt be warmed with an excess of a conc. soln. of chromic acid, it forms a dark red, crystalline mass of **potassium bismuth hydroxydichromate,** $K_2Cr_2O_7.2Bi(OH)(Cr_2O_7)H_2O$. It is decomposed by water.

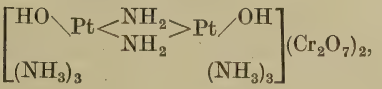
G. Calcagni[17] prepared a hygroscopic, amorphous paste of **chromium dichromate,** $Cr_2(Cr_2O_7)_3$, by evaporating a soln. of chromic oxide in chromic acid. P. Pfeiffer prepared **chromic trisethylenediaminodichromate,** $[Cr\ en_3]_2(Cr_2O_7)_3.2H_2O$, by the action of potassium dichromate on a soln. of the chloride. The yellow needles are slightly soluble in cold water. The salt is decomposed by heat or by exposure to sunlight. O. T. Christensen obtained **chromic nitritopentamminodichromate,** $[Cr(NH_3)_5NO_2]Cr_2O_7$, analogous to the chromate (*q.v.*). A. Werner and J. von Halban made **chromic thiocyanatopentamminodichromate,** $[Cr(NH_3)_5SCy]Cr_2O_7$, in an analogous manner. E. Wilke-Dörfurt and H. G. Mureck prepared **chromic hexantipyrinodichromate,** $[Cr(C_{10}H_{12}N_2)_6](Cr_2O_7)_3$. W. J. Sell, and E. Wilke-Dörfurt and K. Niederer prepared **chromic hexacarbamidodichromate,** $[Cr(CON_2H_4)_6]_2(Cr_2O_7)_3.3H_2O$, as well as **chromic hexacarbamidoperchloratodichromate,** $[Cr(CON_2H_4)_6](Cr_2O_7)ClO_4$; **chromic hexacarbamidodisulphatodichromate,** $[Cr(CON_2H_4)_6]_2(Cr_2O_7)(SO_4)_2.5H_2O$; **chromic hexacarbamidonitratodichromate,** $[Cr(CON_2H_4)_6](NO_3)(Cr_2O_7).H_2O$; **chromic chlorodichromate,** $[Cr(CON_2H_4)_6](Cr_2O_7)Cl.2H_2O$; and **chromic hexacarbamidobromodichromate,** $[Cr(ON_2H_4)_6](Cr_2O_7)Br.H_2O$. They also made **chromic hexacarbamidotetraborofluodichromate,** $[Cr(CON_2H_4)_6]_2(Cr_2O_7)(BF_4)_4$, but not $[Cr(CON_2H_4)_4](Cr_2O_7)BF_4$. G. Calcagni prepared **molybdenum dichromate,** $Mo(Cr_2O_7)_3$, as in the case of the chromium salt; but neither **tungsten dichromate,** nor **uranium dichromate** could be so prepared.

According to M. Gröger,[18] **manganese dichromate,** $MnCr_2O_7$, has not been prepared, but N. Parravano and A. Pasta obtained a complex salt with aniline; and with pyridine. S. H. C. Briggs also prepared a complex with pyridine. According to S. Husain and J. R. Partington, chromic acid acting on an excess of solid manganese carbonate yields a dark red soln. probably containing manganese dichromate. Only partly decomposed solid products could be obtained from this soln. Attempts to prepare double manganese dichromate and potassium chromate were not successful, because the latter is converted into dichromate with the precipitation of manganese dioxide. G. Calcagni prepared **ferric oxybisdichromate,** $Fe_2O(Cr_2O_7)_2$, or $(FeCr_2O_7)_2O$, from a soln. of ferric hydroxide in chromic acid. According to S. Husain and J. R. Partington, the prolonged action of a soln. of chromic acid on an excess of precipitated ferric hydroxide at 80° to 90°, yielded a soln., which, on evaporation at 90°, gave a residue with the composition of **ferric dichromate,** $Fe_2(Cr_2O_7)_3$, after it had been dried in vacuo. Ferric dichromate is a hygroscopic, brown solid which hydrolyzes when the aq. soln. is largely diluted. It decomposes a little at 100°, and at 140° the chromate radicle is decomposed, forming a black residue which slowly dissolves in boiling, conc. hydrochloric acid, forming a green soln. E. Wilke-Dörfurt and H. G. Mureck prepared ferric hexantipyrinodichromate, $[Fe(C_{10}H_{12}N_2)_6](Cr_2O_7)_3$.

J. Schulze[19] obtained a soln. of **cobalt dichromate,** by dissolving cobaltous oxide in a soln. of chromic acid. The liquid contained $CoO : CrO_3$ in the molar ratio 1 : 2. G. Krüss and O. Unger obtained **ammonium cobaltous dichromate,** $(NH_4)_2Cr_2O_7.CoCr_2O_7.2H_2O$, by evaporating in vacuo a hot conc. soln. of equimolar parts of ammonium dichromate and cobalt nitrate. The black, tabular crystals lose their water of crystallization at 105°. O. W. Gibbs prepared **cobaltic hexamminodichromate,** $[Co(NH_3)_6]_2(Cr_2O_7)_3.nH_2O$, in orange needles, by adding ammonium dichromate to a conc. soln. of the nitrate of the base. A. Werner and K. Dawe prepared **cobaltic bispropyldiaminodiamminodichromate,** $[Copn_2(NH_3)_2]_2(Cr_2O_7)_3.2H_2O$; and O. W. Gibbs, **cobaltic aquopentamminodichromate,** $[Co(NH_3)_5(H_2O)]_2(Cr_2O_7)_3.3H_2O$, by adding potassium dichromate to an aq. soln. of the nitrate. O. W. Gibbs also obtained **cobaltic nitritopentamminodichromate,** $[Co(NH_3)_5NO_2]Cr_2O_7$, by adding potassium dichromate to the corresponding nitrate ; the orange-yellow, crystalline precipitate may be crystallized from water acidified with acetic acid. S. M. Jörgensen obtained **cobaltic cisdinitritotetramminodichromate,** $[Co(NH_3)_4(NO_2)_2]_2Cr_2O_7$, as in the case of the corresponding monochromate ; so also with **cobaltic transdinitritotetramminodichromate,** prepared by O. W. Gibbs ; with **cobaltic nitratopentamminodichromate,** $[Co(NH_3)_5NO_3]Cr_2O_7.H_2O$, prepared by S. M. Jörgensen, and O. W. Gibbs ; with **cobaltic chloropentamminodichromate,** $[Co(NH_3)_5Cl]_2Cr_2O_7$, obtained by S. M. Jörgensen ; with **cobaltic iodopentamminodichromate,** $[Co(NH_3)_5I]_2Cr_2O_7$, prepared by A. Werner ; with **cobaltic dichlorotetramminodichromate,** $[Co(NH_3)_4Cl_2]_2Cr_2O_7$, prepared by A. Werner and A. R. Klein—G. Vortmann regarded the salt as *monohydrated ;* and with A. Werner and A. A. Wolberg's **cobaltic dibromotetramminodichromate,** $[Co(NH_3)_4Br_2]_2Cr_2O_7$. G. Vortmann prepared **cobaltic dioxydecamminodichromate,** $[CoO_2(NH_3)_{10}]_2(Cr_2O_7)_5.8H_2O$, from soln. of the chloride and potassium dichromate. P. Ray and P. V. Sarkar obtained **cobaltic chromatotetramminodichromate,** $[Co(NH_3)_4(CrO_4)]_2Cr_2O_7.H_2O$, by the action of chromic acid on the carbonatotetramminonitrate—it loses its water over sulphuric acid ; S. H. C. Briggs obtained the dihydrate by the action of potassium dichromate on a soln. of diaquotetramminonitrate. P. Ray and P. V. Sarkar found that **cobaltic dichromatotetramminodichromate,** $[Co(NH_3)_4(Cr_2O_7)]_2Cr_2O_7.H_2O$, is formed if a larger proportion of chromic acid be employed. P. Ray and P. V. Sarkar also prepared **cobaltic dichromatopentamminochromate,** $[Co(NH_3)_5(Cr_2O_7)]_2CrO_4.3H_2O$; from the corresponding carbonato-salts. S. H. C. Briggs prepared **cobaltic chromatoaquotriamminodichromate,** $[Co(NH_3)_3(H_2O)CrO_4]_2Cr_2O_7.2H_2O$, from soln. of cobalt trinitratotriammine and of sodium dichromate. P. Ray and P. V. Sarkar found that when cobaltic chromatopentamminochromate is recrystallized from dil. acetic acid, it furnishes **cobaltic aquopentamminochromatobisdichromate,** $[Co(NH_3)_5(H_2O)]_2(CrO_4)(Cr_2O_7)_2.H_2O$. S. H. C. Briggs added a cobaltic diaquotetrammino-salt to a large excess of sodium dichromate and obtained brownish-black crystals of **cobaltic enneamminodichromate,** $Co_2(Cr_2O_7)_3.9NH_3.4H_2O$.

S. H. C. Briggs[20] prepared **nickel dichromate,** $NiCr_2O_7.1\frac{1}{2}H_2O$, by boiling on an oil-bath 5·5 grms. of nickel carbonate (with 70 per cent. NiO), with a soln. of 10·5 grms. of chromium trioxide in 7·5 c.c. of water in a flask fitted with a reflux condenser. The crystalline powder has the colour of silver chromate. It deliquesces in air ; and is slowly dissolved by cold water, but rapidly by hot water. G. Chiavarino studied the ethylendiamine salt $NiCr_2O_7.3C_2H_4(NH_2)_2$.

G. B. Buckton[21] prepared **platinous tetramminodichromate,** $Pt[(NH_3)_4]Cr_2O_7$, by treating a soln. of the chloride with chromic acid, and the product drying in vacuo. When crystallized from hot soln. it resembles lead monochromate. It gives off water, ammonia, and nitrogen when heated, leaving platinum, and chromic oxide as a residue. It is sparingly soluble in water; insoluble in alcohol; and when boiled with alcohol and hydrochloric acid it forms aldehyde, chromic chloride, and platinic dichlorotetramminochloride. S. G. Hedin obtained **platinic sulphatotetrapyridinodichromate,** $[Pt(C_5H_5N)_4(SO_4)]Cr_2O_7$, by the method used for the corresponding chromate (*q.v.*). O. Carlgren and P. T. Cleve prepared **platinic dinitritotetramminodichromate,** $[Pt(NH_3)_4(NO_2)_2]Cr_2O_7$, by the action of hydrogen dioxide on the precipitate obtained by mixing soln. of platinous tetramminochloride and potassium dichromate. The lemon-yellow powder detonates when heated. P. T. Cleve prepared **platinic dinitratotetramminodichromate,** $[Pt(NH_3)_4(NO_3)_2]Cr_2O_7$ by the method used for the corresponding chromate; and likewise with **platinic dichlorotetramminodichromate,** $[Pt(NH_3)_4Cl_2]Cr_2O_7$. He also obtained **platinic hydroxyacetatotetramminodichromate,** $[Pt(NH_3)_4(HO)(CH_3COO)]Cr_2O_7.H_2O$, in orange-yellow, six-sided plates from the corresponding chloride and potassium dichromate. He also made **platinic hydroxysulphatotetramminodichromate,** $[Pt(NH_3)_4(OH)(SO_4)]_2Cr_2O_7$, in a similar way; likewise also with **platinic hydroxychlorotetramminodichromate,** $[Pt(NH_3)_4(OH)Cl]Cr_2O_7$. P. T. Cleve obtained **platinic dihydroxydiamidohexamminodichromate,**



$$\left[\begin{matrix} HO\diagdown Pt<{NH_2 \atop NH_2}>Pt\diagup OH \\ (NH_3)_3 \qquad\qquad (NH_3)_3 \end{matrix}\right](Cr_2O_7)_2,$$

as an orange-red precipitate from the corresponding nitrate and potassium dichromate.

REFERENCES.

[1] F. W. Clarke, *Amer. Journ. Science*, (3), **14**. 281, 1877; A. A. Hayes, *ib.*, (2), **20**. 409, 1855; A. Naumann and A. Rücker, *Journ. prakt. Chem.*, (2), **74**. 249, 1906; A. Naumann, *Ber.*, **37**. 4328, 1904; **47**. 1370, 1914; E. Jäger and G. Krüss, *ib.*, **22**. 2036, 1889; H. J. Brooke, *Ann. Phil.*, **22**. 287, 1823; E. Maumené, *Bull. Soc. Chim.*, (3), **7**. 174, 1892; H. Moser, *Chemische Abhandlung über das Chrom*, Wien, 1824; *Schweigger's Journ.*, **42**. 99, 1824; J. S. Abel, *Journ. Chem. Soc.*, **3**. 199, 1850; J. S. Abel and H. Richmond, *ib.*, **3**. 6, 1857; W. C. Ball, *ib.*, **95**. 87, 1909; S. Darby, *ib.*, **1**. 24, 1849; *Liebig's Ann.*, **65**. 205, 1848; H. Schiff, *ib.*, **110**. 74, 1859; C. N. Hinshelwood and E. J. Bowen, *Proc. Roy. Soc.*, **99**. A, 203, 1922; *Phil. Mag.*, (6), **40**. 569, 1920; F. A. H. Schreinemakers, *Zeit. phys. Chem.*, **55**. 71, 1906; *Chem. Weekl.*, **1**. 395, 1905; W. P. Jorissen, *ib.*, **24**. 294, 1927; W. P. Jorissen and G. M. A. Kayser, *Zeit. phys. Chem.*, **130**. 482, 1927; B. Reinitzer, *Zeit. angew. Chem.*, **26**. 456, 1913; C. F. Rammelsberg, *Pogg. Ann.*, **118**. 158, 1863; A. Maus, *ib.*, **9**. 127, 1827; **11**. 83, 1827; K. F. Slotte, *Wied. Ann.*, **14**. 18, 1881; E. Moles and F. Gonzalez, *Anal. Fis. Quim.*, **21**, 204, 1923; M. Berthelot, *Ann. Chim. Phys.*, (6), **1**. 93, 1884; (5), **17**. 833, 1879; *Thermochimie*, Paris, **1**. 282, 1897; *Compt. Rend.*, **96**. 400, 541, 1883; P. Sabatier, *ib.*, **103**. 49, 267, 1886; A. Duffour, *ib.*, **156**. 1022, 1913; F. Morges, *ib.*, **86**. 1443, 1878; S. Schlivitch, *ib.*, **182**. 891, 1926; R. Böttger, *Journ. prakt. Chem.*, (1), **103**. 314, 1867; *Liebig's Ann.*, **47**. 339, 1843; M. Siewert, *Zeit. ges. Naturw.*, **19**. 19, 1862; A. J. Weiss, *Sitzber. Akad. Wien*, **37**. 371, 1859; R. Segalle, *Jahresb. Oberrealschule Czernowitz*, **41**. 1, 1905; G. N. Wyrouboff, *Bull. Soc. Min.*, **13**. 306, 1890; A. Levy, *Pharm. Viertlj.*, **20**. 137, 1870; J. Schabus, *Sitzber. Akad. Wien*, **5**. 369, 1850; *Bestimmung der Krystallgestalten in chemischen Laboratorien erzeugter Produkte*, Wien, 110, 1855; *Pogg. Ann.*, **116**. 420, 1862; W. M. Hooton, *Proc. Chem. Soc.*, **24**. 27, 1908; Y. T. Gerassimoff, *Trans. Inst. Chem. Reagents Moscow*, 6, 1927; *Zeit. anorg. Chem.*, **187**. 321, 1930; B. Gossner and F. Mussgnug, *Zeit. Kryst.*, **72**. 476, 1930,

[2] C. F. Rammelsberg, *Pogg. Ann.*, **128**. 322, 1866; A. Heydweiller, *Zeit. anorg. Chem.*, **116**. 42, 1921; L. Schulerud, *Journ. prakt. Chem.*, (2), **19**. 36, 1879; F. A. H. Schreinemakers, *Chem. Weekbl.*, **2**. 633, 1905; *Zeit. phys. Chem.*, **55**. 71, 1906; Y. T. Gerassimoff, *Trans. Inst. Chem. Reagents Moscow*, 6, 1927; *Zeit. anorg. Chem.*, **187**. 321, 1930.

[3] M. Siewert, *Zeit. ges. Naturwiss.*, **19**. 17, 1862; G. Bessa, *Ind. Chim.*, **9**. 143, 1922; *Chem. Trade Journ.*, **70**. 595, 1922; R. Kissling, *Chem. Ztg.*, **15**. 373, 1891; H. Moser, *Chemische Abhandlung über das Chrom*, Wien, 1824; *Schweigger's Journ.*, **42**. 99, 1824; J. Thomsen, *Thermochemische Untersuchungen*, Leipzig, **1**. 255, 1882; A. Stanley, *Chem. News*. **54**. 194, 1886; F. Morges, *Compt. Rend.*, **86**. 1443, 1878; L. J. Simon, *ib.*, **178**. 1606, 1924; H. Ollivier, *ib.*, **186**. 1001, 1928; A. Poirot, *ib.*, **189**. 150, 1929; M. Berthelot, *ib.*, **96**. 542, 1883; *Ann. Chim. Phys.*, (6), **1**. 92, 1884; *Thermochimie*, Paris, **1**. 282, 1897; I. Traube, *Ber.*, **24**. 3078, 1891; F. Mylius and R. Funk, *Abh. Phys. Tech. Reichsanst.* **3**. 456, 1900; *Ber.*, **33**. 3688, 1900; F. Rüdorff, *ib.*, **21**. 3047, 1888; Y. I. Gerassimoff, *Zeit. anorg. Chem.*, **187**. 321, 1930; H. Pincass,

Continental Met. Chem. Eng., **2**. 233, 1927 ; F. A. H. Schreinemakers, *Chem. Weekbl.*, **2**. 211, 1905 ; *Zeit. phys. Chem.*, **55**. 91, 1906 ; P. Walden, *ib.*, **2**. 71, 1888 ; E. Müller and E. Sauer, *Zeit. Elektrochem.*, **18**. 844, 1912 ; E. Müller, *ib.*, **32**. 399, 1926 ; I. Stsherbakoff, *ib.*, **32**. 396, 1926 ; A. Lottermoser and K. Falk, *ib.*, **28**. 366, 1922 ; H. C. Jones, *Hydrates in Aqueous Solution*, Washington, 38, 1907 ; H. C. Jones and H. P. Bassett, *Amer. Chem. Journ.*, **34**. 318, 1905 ; C. Watkins and H. C. Jones, *Journ. Amer. Chem. Soc.*, **37**. 2626, 1915 ; T. W. Richards and G. L. Kelley, *ib.*, **33**. 847, 1911 ; *Proc. Amer. Acad.*, **47**. 171, 1911 ; P. L. Robinson, G. E. Stephenson and H. V. A. Briscoe, *Journ. Chem. Soc.*, **127**. 547, 1925 ; A. Naumann, *Ber.*, **37**. 4328, 1904 ; G. N. Wyrouboff, *Bull. Soc. Min.*, **14**. 77, 1891 ; H. Dufet, *ib.*, **13**. 341, 1890 ; L. Münzing, *Zeit. Kryst.*, **14**. 62, 1888 ; B. Reinitzer, *Zeit. angew. Chem.*, **26**. 456, 1913 ; E. C. Franklin and C. A. Kraus, *Amer. Chem. Journ.*, **20**. 829, 1898 ; J. d'Ans and J. Löffler, *Ber.*, **63**. B, 1446, 1930 ; V. K. la Mer and C. L. Read, *Journ. Amer. Chem. Soc.*, **52**. 3098, 1930 ; B. Neumann and C. Exssner, *Zeit. angew. Chem.*, **43**. 440, 1930.

[4] M. Kimura, *Mem. Coll. Kyoto*, **4**. 173, 1920 ; E. Forster, *Untersuchungen über die Beziehungen zwischen dem specifischen Brechungsversmögen und der Concentration von Salzlösungen*, Bern, 1878 ; S. F. Schemtschuschny, *Journ. Russ. Phys. Chem. Soc.*, **38**. 1135, 1907 ; *Zeit. anorg. Chem.*, **57**. 267, 1908 ; K. Someya, *ib.*, **159**. 158, 1926 ; W. P. Jorissen and G. M. A. Kayser, *Rec. Trav. Chim. Pays-Bas*, **23**. 668, 1927 ; F. Tassaert, *Ann. Chim. Phys.*, (1), **22**. 51, 1823 ; H. V. Regnault, *ib.*, (3), **1**. 166, 1841 ; A. Lallemand, *ib.*, (4), **22**. 200, 1871 ; P. Grouvelle, *ib.*, (2), **17**. 349, 1821 ; P. Berthier, *ib.*, (3), **7**. 1843 ; E. M. Péligot, *ib.*, (2), **52**. 267, 1833 ; (3), **12**. 528, 1844 ; R. T. M. y Luna, *ib.*, (3), **68**. 183, 1863 ; A. Michel and L. Krafft, *ib.*, (3), **41**. 478, 1854 ; H. Jeannel, *ib.*, (4), **6**. 166, 1865 ; *Compt. Rend.*, **61**. 412, 1865 ; **62**. 37, 1866 ; *Mém. Soc. Bordeaux*, **4**. 8, 1866 ; J. N. Rakshit, *Zeit. Elektrochem.*, **31**. 97, 1925 ; J. Schabus, *Sitzber. Akad. Wien*, **5**. 369, 1850 ; *Bestimmung der Krystallgestalten in chemischen Laboratorien erzeugter Produkte*, Wien, 110, 1855 ; *Pogg. Ann.*, **116**. 420, 1862 ; A. Beer, *ib.*, **82**. 429, 1851 ; F. Melde, *ib.*, **124**. 91, 1865 ; J. Müller, *ib.*, **72**. 76, 1847 ; P. Groth, *ib.*, **133**. 193, 1868 ; H. Rose, *ib.*, **27**. 585, 1833 ; **45**. 183, 1838 ; C. F. Rammelsberg, *ib.*, **91**. 353, 1845 ; F. E. Neumann, *ib.*, **126**. 123, 1865 ; E. Mitscherlich, *ib.*, **28**. 120, 1833 ; P. Kremers, *ib.*, **92**. 497, 1854 ; **96**. 39, 63, 1855 ; H. Baumhauer, *ib.*, **140**. 274, 1870 ; *Zeit. deut. geol. Ges.*, **35**. 639, 1883 ; C. Decharne, *Lumière électr.*, **26**. 69, 1887 ; P. L. Robinson, G. E. Stephenson and H. V. A. Briscoe, *Journ. Chem. Soc.*, **127**. 547, 1925 ; H. J. P. Venn and V. Edge, *ib.*, 2142, 1928 ; F. Fichter and E. Brunner, *ib.*, 1862, 1928 ; G. Brügelmann, *Ber.*, **15**. 1833, 1882 ; H. G. F. Schröder, *ib.*, **11**. 2017, 1878 ; *Dichtigkeitsmessungen*, Heidelberg, 1873 ; M. Traube, *Liebig's Ann.*, **66**. 166, 1848 ; I. Traube, *Ber.*, **24**. 3077, 1891 ; A. Naumann, *ib.*, **37**. 4329, 1904 ; **47**. 1370, 1914 ; F. Rüdorff, *ib.*, **21**. 3047, 1888 ; K. Vierordt, *ib.*, **5**. 34, 1872 ; *Die Anwendung des Spectralapparates zur Photometrie*, Tübingen, 1873 ; J. C. G. de Marignac, *Bull. Soc. Chim.*, (2), **41**. 541, 1884 ; E. Montignie, *ib.*, (4), **45**. 492, 1929 ; J. B. Senderens, *ib.*, (3), **6**. 804, 1891 ; (3), **7**. 515, 1892 ; L. Godefroy, *ib.*, (2), **40**. 167, 1883 ; (2), **42**. 194, 1884 ; *Compt. Rend.*, **99**. 141, 1884 ; P. Weiss and P. Collet, *ib.*, **178**. 1890, 1924 ; P. Weiss, *ib.*, **182**. 105, 1926 ; S. Schlivitch, *ib.*, **182**. 891, 1926 ; H. Dufet, *Bull. Soc. Min.*, **13**. 199, 341, 1890 ; G. N. Wyrouboff, *ib.*, **13**. 306, 1890 ; Y. R. Goldstein, *Journ. Russ. Chem. Ind.*, 564, 1926 ; A. Kailan, *Anz. Akad. Wien*, **61**. 161, 1924 ; G. Meslin, *Ann. Chim. Phys.*, (8), **7**. 145, 1906 ; *Compt. Rend.*, **140**. 782, 1905 ; H. le Chatelier, *ib.*, **118**. 350, 1894 ; F. Morges, *ib.*, **86**. 1443, 1878 ; M. Alluard, *ib.*, **59**. 500, 1864 ; A. Étard, *ib.*, **120**. 1058, 1895 ; *Ann. Chim. Phys.*, (7), **2**. 550, 1894 ; M. Berthelot, *ib.*, (6), **1**. 92, 1884 ; *Compt. Rend.*, **96**. 399, 542, 1880 ; P. Nordmeyer and A. L. Bernoulli, *Ber. deut. phys. Ges.*, **5**. 175, 1907 ; A. C. Robertson, *Proc. Nat. Acad.*, **13**. 192, 1927 ; *Journ. Amer. Chem. Soc.*, **49**. 1630, 1927 ; W. Hempel and C. Schubert, *Zeit. Elektrochem.*, **17**. 729, 1912 ; C. Schubert, *Beiträge zur Kenntnis der Dissoziation einiger Oxyde, Karbonate und Sulfide*, Weida i. Th., 35, 1910 ; H. Kopp, *Liebig's Ann. Suppl.*, **3**. 296, 1865 ; H. Schiff, *Liebig's Ann.*, **110**. 74, 1859 ; **126**. 171, 1863 ; A. Reinecke, *ib.*, **126**. 113, 1863 ; H. Buff, *ib.*, **110**. 257, 1859 ; O. Popp, *ib.*, **156**. 90, 1870 ; E. Viterhi and G. Krautz, *Gazz. Chim. Ital.*, **57**. 690, 1927 ; J. B. Ferguson, *Journ. Washington Acad.*, **15**. 279, 1925 ; A. Hettich and A. Schleede, *Zeit. Physik*, **50**. 249, 1928 ; E. Heyn and O. Bauer, *Mitt. Materialprüf. Amt.*, **26**. 1, 1907 ; H. P. Cady and R. Taft, *Journ. Phys. Chem.*, **29**. 1057, 1075, 1925 ; G. B. Frankforter, V. H. Rochrich and E. V. Manuel, *Journ. Chem. Soc.*, **98**. ii, 292, 1910 ; B. K. Mukerji, A. K. Bhattacharji and N. R. Dhar, *Journ. Phys. Chem.*, **32**. 1834, 1928 ; *Journ. Amer. Chem. Soc.*, **32**. 178, 1910 ; W. K. van Haagen and E. F. Smith, *ib.*, **33**. 1505, 1911 ; M. S. Sherrill, *ib.*, **29**. 1641, 1907 ; R. L. Datta and N. R. Dhar, *ib.*, **38**. 1303, 1917 ; R. G. van Name and F. Fenwick, *ib.*, **47**. 19, 1925 ; H. C. Jones and W. W. Strong, *Phys. Zeit.*, **10**. 499, 1909 ; *A Study of Absorption Spectra*, Washington, 1910 ; H. C. Jones and C. A. Jacobson, *Amer. Chem. Journ.*, **40**. 355, 1908 ; A. P. West and H. C. Jones, *ib.*, **44**. 508, 1910 ; H. G. Leopold and J. Johnston, *Journ. Amer. Chem. Soc.*, **49**. 1974, 1927 ; H. G. Greenish and F. A. U. Smith, *Pharm. Journ.*, (4), **66**. 774, 1901 ; E. F. Anthon, *Repert. Pharm.*, (2), **9**. 346, 1837 ; W. Spring, *Bull. Soc. Chim. Belg.*, **24**. 109, 1910 ; *Bull. Acad. Belg.*, 11, 1910 ; *Rec. Trav. Chim. Pays-Bas*, **29**. 163, 1910 ; *Arch. Sciences Genève*, (4), **29**. 145, 1910 ; E. S. Hedges, *Nature*, **123**. 837, 1929 ; E. N. Gapon, *Ukraine Chem. Journ.*, **4**. 161, 1929 ; E. V. Murphree, *Journ. Ind. Eng. Chem.*, **15**. 148, 1923 ; S. Levites, *Koll. Zeit.*, **9**. 1, 1911 ; M. le Blanc, *Zeit. phys. Chem.*, **86**. 335, 1913 ; A. Eucken and G. Kuhn, *ib.*, **133**. 193, 1928 ; M. le Blanc and W. Schmandt, *Zeit. Elektrochem.*, **16**. 114, 1910 ; R. Marc, *ib.*, **16**. 201, 1910 ; *Zeit. phys. Chem.*, **67**. 470, 1910 ; H. von Halban and K. Siedentopf, *ib.*, **100**. 208, 1922 ; W. P. Jorissen and G. W. A. Kayser, *ib.*, **130**. 482, 1927 ; W. P. Jorissen, *Chem. Weekbl.*, **21**. 294, 1927 ; H. A. Miers, *Min. Mag.*, **15**. 39, 1909 ; *Science*

Progress, (2), **2**. 121, 1907 ; L. Kahlenberg and W. J. Trautmann, *Trans. Amer. Electrochem. Soc.*, **39**. 377, 1921 ; F. Rinne, *Neues Jahrb. Min.*, i, 171, 1900 ; D. N. Arteméeff, *Zeit. Kryst.*, **54**. 174, 1914 ; A. Schubnikoff, *ib.*, **50**. 19, 1911 ; L. Stibing, *ib.*, **41**. 611, 1906 ; A. Fock, *ib.*, **23**. 216, 1894 ; O. Lehmann, *ib.*, **5**. 613, 1881 ; *Molekularphysik*, Leipzig, **1**. 172, 1888 ; F. Flöttmann, *Zeit. anal. Chem.*, **73**. 1, 1928 ; W. Eidmann, *Ein Beitrag zur Erkenntnis des Verhaltens chemischer Verbindungen in nichtwässrigen Lösungen*, Giessen, 1899 ; J. Formanek, *Die qualitative Spectralanalyse anorganischer Körper*, Berlin, 1900 ; W. Böhlendorff, *Studien zur Absorptionsspectral analyse*, Erlangen, 1890 ; H. Bremer, *Einfluss der Temperatur gefärbter Lösungen auf die Absorptionsspectra derselben*, Erlangen, 1890 ; J. M. Hiebendaal, *Onderzoek over eenige absorptiespectra*, Utrecht, 1873 ; H. B. Weiser and E. B. Middleton, *Journ. Phys. Chem.*, **24**. 630, 1920 ; N. Ishizaka, *Zeit. phys. Chem.*, **83**. 197, 1913 ; S. Berkman and H. Zocker, *ib.*, **124**. 318, 1926 ; M. Volmer and A. Weber, *ib.*, **119**. 277, 1926 ; T. Svensson, *Arkiv Kemi Min.Geol.*, **7**. 19, 1919 ; *Lichtelektrische Untersuchungen au Salzlösungen*, Stockholm, 58, 1919 ; L. R. Ingersoll, *Journ. Amer. Opt. Soc.*, **6**. 663, 1922 ; C. F. Cross, *Chem. News*, **44**. 210, 1881 ; E. Kopp, *ib.*, **9**. 278, 1864 ; S. Kern, *ib.*, **33**. 236, 1876 ; D. Lindo, *ib.*, **58**. 29, 1888 ; T. Thomson, *Ann. Phil.*, **16**. 321, 1820 ; R. T. Thomson, *Chem. News*, **52**. 59, 1885 ; H. M. Vernon, *ib.*, **66**. 104, 114, 141, 152, 1892 ; L. Playfair and J. P. Joule, *Mem. Chem. Soc.*, **2**. 401, 1845 ; *Journ. Chem. Soc.*, **1**. 137, 1849 ; E. J. Bowen and C. W. Bunn, *ib.*, 2353, 1927 ; J. A. Wilson, *Chem. Trade Journ.*, **6**. 92, 1890 ; C. J. B. Karsten, *Schweigger's Journ.*, **65**. 394, 1832 ; G. Rössler, *Ber.*, **59**. B, 2606, 1926 ; F. A. H. Schreinemakers, *Chem. Weekbl.*, **1**. 837, 1905 ; *Zeit. phys. Chem.*, **55**. 71, 1906 ; E. von Stackelberg, *ib.*, **26**. 543, 1898 ; A. Kanitz, *ib.*, **22**. 336, 1897 ; W. Ostwald, *ib.*, **2**. 78, 1888 ; A. Speransky, *ib.*, **78**. 86, 1911 ; O. Hauser and H. Herzfeld, *ib.*, **68**. 175, 1910 ; R. Lorenz and H. T. Kalmus, *ib.*, **59**. 30, 251, 1907 ; P. Walden, *ib.*, **1**. 547, 1887 ; **2**. 71, 1881 ; R. Abegg and A. T. Cox, *ib.*, **48**. 725, 1904 ; W. C. D. Whetham, *ib.*, **11**. 220, 1893 ; *Proc. Roy. Soc.*, **66**. A, 192, 1900 ; **71**. A, 332, 1903 ; T. G. Bedford, *ib.*, **83**. A, 454, 1910 ; I. Koppel and E. Blumenthal, *Zeit. anorg. Chem.*, **53**. 263, 1907 ; R. Lorenz and W. Herz, *ib.*, **120**. 322, 1922 ; **135**. 374, 1924 ; **138**. 330, 1924 ; W. Herz, *ib.*, **170**. 238, 1928 ; J. Lundberg, *ib.*, **55**. 433, 1907 ; J. Sand and K. Kästle, *ib.*, **52**. 101, 1907 ; E. Groschuff, *ib.*, **58**. 102, 1908 ; E. Spitalsky, *ib.*, **54**. 265, 1907 ; J. Thomsen, *Thermochemische Untersuchungen*, Leipzig, **1**. 255, 1882 ; *Journ. prakt. Chem.*, (2), **17**. 165, 1878 ; H. Reinsch, *ib.*, (2), **28**. 371, 1843 ; A. Michaelis, *ib.*, (2), **4**. 352, 1871 ; F. Bothe, *ib.*, (1), **46**. 184, 1849 ; C. von Hauer, *ib.*, (1), **103**. 118, 1868 ; *Sitzber. Akad. Wien*, **53**. 221, 1866 ; F. Fouqué, *Ann. Obs. Paris*, **9**. 172, 1868 ; *Compt. Rend.*, **64**. 121, 1867 ; P. Sabatier, *Journ. Phys.*, (2), **6**. 312, 1887 ; *Compt. Rend.*, **103**. 49, 1886 ; P. Bary, *ib.*, **114**. 827, 1892 ; A. Duffour, *ib.*, **156**. 1022, 1913 ; **159**. 260, 1914 ; L. J. Simon, *ib.*, **178**. 1606, 1924 ; L. Santi, *Bull. Chim. Farm.*, **43**. 673, 1904; K. F. Slotte, *Wied. Ann.*, **14**. 18, 1881 ; H. Settegast, *ib.*, **7**. 242, 1879 ; G. Quincke, *ib.*, **24**. 347, 1885 ; **34**. 401, 1888 ; O. Knoblauch, *ib.*, **43**. 751, 1891 ; F. Guthrie, *Phil. Mag.*, (4), **49**. 18, 367, 1875 ; (5), **17**. 470, 1884 ; J. H. Gladstone, *Proc. Roy. Soc.*, **16**. 439, 1868 ; *Phil. Mag.*, (4), **36**. 311, 1868 ; W. H. Balmain, *ib.*, (3), **21**. 270, 1842 ; J. A. Ewing and J. G. MacGregor, *Trans. Roy. Soc. Edin.*, **27**. 51, 1872 ; C. P. Smyth, *ib.*, **28**. 779, 1879 ; F. Grünbaum, *Zur. Photometric der Absorptionsspektren von Lösungen*, Berlin, 1903 ; *Ann. Physik*, (4), **12**. 1010, 1903 ; R. von Sahmen and G. Tammann, *ib.*, (4), **10**. 879, 1903 ; G. Tammann, *Kristallisieren und Schmelzen*, Leipzig, 262, 1903 ; G. Tammann and Q. A. Mansuri, *Zeit. anorg. Chem.*, **126**. 119, 1923 ; A. Heydweiller, *ib.*, **116**. 42, 1921 ; J. Morland, *Journ. Chem. Soc.*, **13**. 252, 1860 ; E. A. Parnell, *ib.*, **21**. 356, 1868 ; H. Bassett, *ib.*, **83**. 692, 1903 ; J. W. Thomas, *ib.*, **33**. 367, 1878 ; E. J. Bowen and E. T. Yarnold, *ib.*, 1648, 1929 ; A. F. Hallimond, *Min. Mag.*, **21**. 277, 1927 ; T. Graham, *Phil. Mag.*, (3), **22**. 329, 1843 ; (3), **24**. 401, 1844 ; H. S. Roberts, *Phys. Rev.*, (2), **23**. 386, 1924 ; J. A. Fleming and J. Dewar, *Proc. Roy. Soc.*, **61**. 380, 1897 ; L. A. Welo and A. Baudisch, *Nature*, **116**. 606, 1925 ; T. G. Gentele, *Oefvers. Vet. Akad. Förh.*, 4, 1851 ; K. S. Gibson, *Journ. Amer. Opt. Soc.*, **9**. 113, 1924 ; K. Brückner, *Monatsh.*, **27**. 199, 1906 ; G. P. Vincent, *Journ. Phys. Chem.*, **29**. 875, 1925 ; F. Bush, *ib.*, **31**. 931, 1927 ; H. Schwarz, *Dingler's Journ.*, **186**. 31, 1867 ; T. Sabalitschka and G. Kubisch, *Pharm. Centrh.*, **65**. 272, 1924 ; A. Commaille, *Journ. Chim. Pharm.*, (4), **11**. 360, 1872 ; F. Margueritte, *ib.*, (3), **27**. 21, 1855 ; W. Kuczynsky, *Rocz. Chem.*, **7**. 397, 1927 ; E. Brentel, *Ber. öester. chem. Ges.*, **14**. 142, 1892 ; *Zeit. anorg. Chem.*, **3**. 84, 1893 ; W. Herz and F. Hiebenthal, *ib.*, **177**. 363, 1929 ; M. Schwarz, *Zeit. Elektrochem.*, **32**. 15, 1926 ; E. Pietsch, A. Kotorsky and G. Behrend, *ib.*, **35**. 582, 1929 ; I. Plotnikoff, *ib.*, **32**. 13, 1926 ; I. Plotnikoff and M. Karsulin, *Zeit. Physik*, **36**. 277, 1926 ; A. Manuelli, *Atti Accad. Lincei*, (5), **15**. i, 703, 1906 ; M. Amadori, *ib.*, (5), **21**. i, 667, 1912 ; (5), **22**. i, 453, 609, 1912 ; A. Sella, *Atti Accad. Torino*, **25**. 153, 1889 ; *Riv. Min. Crist. Ital.*, **6**. 58, 1890 ; A. A. Hayes, *Amer. Journ. Science*, (1), **14**. 136, 1828 ; (1), **20**. 409, 1831 ; V. Ipatieff and A. Kisseleff, *Ber.*, **59**. B, 1418, 1926 ; R. Lenz, *Bull. Acad. St. Petersburg*, (5), **26**. 3, 1878 ; A. Reychler, *Bull. Soc. Chim. Belg.*, **36**. 236, 1925 ; C. Tomlinson, *Proc. Roy. Soc.*, **18**. 533, 1870 ; **20**. 41, 1872 ; **21**. 208, 1873 ; *Phil. Trans.*, **161**. 51, 1871 ; *Phil. Mag.*, (4), **40**. 221, 1870 ; (4), **45**. 385, 1873 ; J. Forrest, *Trans. Roy. Soc. Edin.*, **54**. 601, 1927 ; E. R. Bullock, *Journ. Phys. Chem.*, **28**. 179, 1924 ; C. M. Guldberg, *Foch. Vid. Selsk. Christiania*, 1, 1870 ; F. Weigert, *Zeit. Elektrochem.*, **12**. 377, 1906 ; W. A. Tilden and W. A. Shenstone, *Phil. Trans.*, **175**. 34, 1884 ; J. G. F. Druce, *Pharm. Journ.*, **119**. 333, 1927 ; C. Schaefer and M. Schubert, *Zeit. Physik*, **7**. 297, 1921 ; I. Obreimoff and W. J. de Haas, *Versl. Akad. Amsterdam*, **37**. 31, 1928 ; *Proc. Acad. Amsterdam*, **31**. 353, 1928 ; J. Wagner, *Tabellen zum Einbauchrefraktometer*, Sondershauser, 1907 ; J. Fritzsche, *Mem. Acad. St. Petersburg*, **6**. 181, 1840 ; *Journ. prakt. Chem.*, (1), **19**. 176, 1840 ; *Pogg. Ann.*, **50**. 540, 1840;

G. T. Gerlach, *Zeit. anal. Chem.*, **8**. 288, 1869 ; W. G. Hankel and H. Lindenberg, *Abh. Sächs. Ges. Wien*, **18**. 361, 1892 ; **21**. 11, 1894 ; K. H. Butler and D. McIntosh, *Trans. Roy. Soc. Canada*, (3), **21**. 19, 1927 ; E. C. Franklin and C. A. Kraus, *Amer. Chem. Journ.*, **20**. 829, 1898 ; F. W. O. de Coninck, *Bull. Acad. Belg.*, 257, 1905 ; J. B. Johnson, *Phys. Rev.*, (2), **32**. 97, 1928 ; W. K. Sullivan, *B.A. Rep.*, 66, 1858 ; R. Hunt, *Mem. Chem. Soc.*, **2**. 316, 1845 ; J. C. Witt, *Journ. Amer. Chem. Soc.*, **40**. 1026, 1918 ; M. Neidle and J. C. Witt, *ib.*, **37**. 2360, 1915 ; **38**. 47, 1916 ; J. Piccard and F. de Montmollin, *Helvetica Chim. Acta*, **6**. 1021, 1923 ; J. B. Robertson, *Journ. Soc. Chem. Ind.*, **43**. 334, T, 1924 ; L. A. Welo, *Phil. Mag.*, (7), **6**. 481, 1928 ; A. E. Lindh, *Ark. Mat. Fys.*, **18**. 14, 1924 ; *Compt. Rend.*, **172**. 1175, 1921 ; **175**. 25, 1922 ; *Zeit. Physik*, **6**. 303, 1921 ; **31**. 210, 1925 ; D. Coster, *ib.*, **25**. 83, 1924 ; O. Stelling, *ib.*, **50**. 506, 626, 1928 ; W. Schneider, *ib.* **51**. 266, 1928 ; J. Plotnikoff, *Chem. Ztg.*, **52**. 669, 1928 ; W. R. Hodgkinson and J. Young, *B.A. Rep.*, 676, 1892 ; J. Traube and W. von Behren, *Zeit. phys. Chem.*, **138**. 85, 1928 ; G. Grather and T. Nagahama, *Hokkaido Journ. Agric.*, **24**. 25, 1928 ; R. F. Beard and N. W. Taylor, *Journ. Amer. Chem. Soc.*, **51**. 1973, 1929 ; R. E. de Lury, *Journ. Phys. Chem.*, **7**. 239, 1903 ; G. Kernot and F. Pietrofesa, *Rend. Accad. Napoli*, **3**. 275, 1911 ; T. Murayasu, *Hokkaido Journ. Med.*, **6**. 328, 1928 ; E. Pietsch, A. Kotowsky and G. Berend, *Zeit. phys. Chem.*, **5**. B, 1, 1929 ; E. H. Riesenfeld and O. Hecht, *Zeit. wiss. Photochem.*, **26**. 369, 1929 ; D. S. Morton, *Journ. Phys. Chem.*, **33**. 1135, 1929 ; T. Aden, *Die Aenderungen der Absorptionsspektren im sichtbaren und ultravioletten Gebiet bei Aggregationen in Lösungen schwacher anorganischer Säuren und ihrer Salze*, Göttingen, 1929 ; N. R. Tawde and G. R. Paranjpe, *Indian Journ. Phys.*, **4**. 533, 1930 ; H. Moser, *Chemische Abhandlung über das Chrom*, Wien, 1824 ; *Schweigger's Journ.*, **42**. 99, 1824 ; H. Pincaso, *Continental Met. Chem. Eng.*, **2**. 233, 1927 ; B. Reinitzer, *Zeit. angew. Chem.*, **26**. 456, 1913 ; H. E. Buckley, *Zeit. Kryst.*, **75**. 15, 1930 ; B. Gossner and F. Mussgnug, *ib.*, **72**. 476, 1930 ; M. M. Narkevich, *Journ. Russ. Chem. Ind.*, **6**. 1438, 1929 ; N. A. Izgarischeff and A. K. Belaieff, *Journ. Russ. Phys. Chem. Soc.*, **62**. 249, 1930 ; M. G. Mellon, *Journ. Phys. Chem.*, **33**. 1931, 1929 ; V. S. Yatloff, *Zhur. Prikladnoi Khim.*, **2**. 561, 1929 ; P. L. Stedehouder and P. Terpstra, *Physica*, **10**. 113, 1930 ; J. W. Williams and E. M. Drissen, *Journ. Biol. Chem.*, **87**. 441, 1930 ; E. Pistsch, A. Kotowsky and F. G. Berend, *Zeit. Elektrochem.*, **35**. 582, 1929 ; *Zeit. phys. Chem.*, **5**. B, 1, 1929 ; W. von Behren and J. Traube, *ib.*, **146**. 1, 1930 ; W. V. Bhagwat and N. R. Dhar, *Journ. Indian Chem. Soc.*, **6**. 781, 1929 ; E. Gray, *Rev. Chim. Ind.*, **39**. 2, 39, 104, 230, 1930 ; G. Jander, *Metallbörse*, **20**. 1855, 1930 ; F. Flöttmann, *Ueber Löslichkeitsgleichgewichte*, Marburg, 1928.

[5] L. Grandeau, *Ann. Chim. Phys.*, (3), **67**. 227, 1863 ; *Chem. News*, **6**. 295, 310, 1862 ; G. N. Wyrouboff, *Bull. Soc. Min.*, **4**. 120, 1881 ; **13**. 302, 1890 ; *Bull. Soc. Chim.*, (3), **25**. 118, 1901 ; (4), **3**. 7, 1908 ; W. Stortenbecker, *ib.*, (4), **3**. 481, 1908 ; *Rec. Trav. Chim. Pays-Bas*, **26**. 240, 1907 ; B. Gossner in P. Groth, *Chemische Krystallographie*, Leipzig, **2**. 588, 1908 ; F. A. H. Schreinemakers and A. Filippo, *Chem. Weekbl.*, **3**. 157, 1906 ; J. A. le Bel, *Compt. Rend.*, **153**, 1081, 1911 ; A. F. Hallimond, *Min. Mag.*, **21**. 277, 1927.

[6] C. Chabrié, *Compt. Rend.*, **132**. 680, 1901 ; F. R. Fraprie, *Amer. Journ. Science*, (4), **21**. 309, 1906 ; F. A. H. Schreinemakers and D. J. Meijeringh, *Chem. Weekbl.*, **5**. 811, 1908 ; A. F. Hallimond, *Min. Mag.*, **21**. 277, 1927.

[7] F. Dröge, *Liebig's Ann.*, **101**. 39, 1857 ; A. Viefhaus, *Journ. prakt. Chem.*, (1), **88**. 431, 1863 ; L. Balbiano, *Atti Accad. Lincei*, (4), **4**. 597, 1888 ; *Gazz. Chim. Ital.*, **18**. 195, 1888 ; N. Parravano and A. Pasta, *ib.*, **37**. ii, 255, 1907 ; J. Schulze, *Zeit. anorg. Chem.*, **10**. 150, 1895 ; G. Krüss and O. Unger, *ib.*, **8**. 455, 1895 ; M. Gröger, *ib.*, **66**. 7, 1910 ; A. and L. Lumière and A. Seyewetz, *Bull. Soc. Chim.*, (3), **33**. 1040, 1905 ; A. Stanley, *Chem. News*, **54**. 196, 1886 ; C. Freese, *Pogg. Ann.*, **140**. 77, 1869 ; F. Zambonini, *Zeit. Kryst.*, **47**. 620, 1910.

[8] A. Janek, *Koll. Chem. Beihefte*, **24**. 418, 1927 ; R. Warington, *Phil. Mag.*, (3), **11**. 489, 1837 ; L. N. Vauquelin, *Ann. Chim. Phys.*, (1), **70**. 70, 1809 ; H. Moser, *Chemische Abhandlung über das Chrom*, Wien, 1824 ; *Schweigger's Journ.*, **42**. 99, 1824 ; G. Krüss, *Zeit. anorg. Chem.*, **8**. 456, 1895 ; E. Jäger and G. Krüss, *Ber.*, **22**. 2050, 1889 ; W. Autenrieth, *ib.*, **35**. 2057, 1902 ; O. Mayer, *ib.*, **36**. 1740, 1903 ; E. R. Riegel and M. C. Reinhard, *Journ. Phys. Chem.*, **31**. 713, 1927 ; C. Freese, *Pogg. Ann.*, **140**. 77, 1869 ; J. W. Retgers, *Zeit. phys. Chem.*, **8**. 52, 1891 ; M. S. Sherrill, *Journ. Amer. Chem. Soc.*, **29**. 1641, 1907 ; M. S. Sherrill and D. F. Russ, *ib.*, **29**. 1673, 1907 ; M. S. Dunin and F. M. Shemyakin, *Koll. Zeit.*, **39**. 50, 1926 ; G. H. Zeller, *Repert. Pharm.*, **71**. 250, 1840 ; A. Helmsauer, *ib.*, **38**. 105, 1831 ; E. Spitalsky, *Journ. Russ. Phys, Chem. Soc.*, **46**. 566, 1914 ; S. Darby, *Journ. Chem. Soc.*, **1**. 24, 1849 ; *Liebig's Ann.*, **65**. 204, 1848 ; H. G. F. Schröder, *Dichtigkeitsmessungen*, Heidelberg, 1873 ; *Liebig's Ann.*, **172**. 298, 1874 ; **173**. 72, 1874 ; **174**. 249, 1874 ; J. Schabus, *Sitzber. Akad. Wien*, **5**. 369, 1850 ; *Bestimmung der Krystallgestalten in chemischen Laboratorien erzeugter Produkte*, Wien, 110, 1855 ; *Pogg. Ann.*, **116**. 420, 1862 ; R. G. van Name and R. S. Bothworth, *Zeit. anorg. Chem.*, **67**. 97, 1910 ; *Amer. Journ. Science*, (4), **29**. 293, 1910 ; F. Köhler, *Zeit. anorg. Chem.*, **96**. 207, 1916 ; S. H. C. Briggs, *ib.*, **56**. 258, 1908 ; G. P. Baxter and R. H. Jess, *ib.*, **62**. 331, 1909 ; *Journ. Amer. Chem. Soc.*, **31**. 541, 1909 ; G. P. Baxter, M. A. Hines, and E. Mueller, *ib.*, **31**. 529, 1909 ; *Zeit. anorg. Chem.*, **62**. 313, 1909 ; P. Ray and J. Dasgupta, *Journ. Indian Chem. Soc.*, **5**. 519, 1928 ; D. Audalian, *Ukrain. Khem. Zhur.*, **3**. 223, 1928 ; F. B. Hofmann, *Zeit. phys. Chem.*, **83**. 385, 1913 ; E. F. Teschemaker, *Phil. Mag.*, **2**. 345, 1827 ; E. S. Hedges and R. V. Henley, *Journ. Chem. Soc.*, 2714, 1928 ; E. S. Hedges, *Journ. Soc. Chem. Ind.—Chem. Ind.*, **47**. 710, 1928.

[9] A. Dalzell, *B.A. Rep.*, 68, 1859 ; K. Preis and B. Rayman, *Ber.*, **13**. 340, 1880 ; W. Autenrieth, *ib.*, **35**. 2062, 1902 ; O. Mayer, *ib.*, **36**. 1742, 1903 ; F. Mylius and J. von Wrochem, *ib.*,

33. 3689, 1900; A. Naumann, *ib.*, **37**. 4328, 1904; G. N. Wyrouboff, *Bull. Soc. Min.*, **14**. 77, 1891; J. F. Bahr, *Oefvers. Akad. Förh.*, **9**. 155, 1852; *Journ. prakt. Chem.*, (1), **60**. 60, 1853; L. Schulerud, *ib.*, (2), **19**. 38, 1879; L. N. Vauquelin, *Ann. Chim. Phys.*, (1), **70**. 70, 1889; E. Zettnow, *Pogg. Ann.*, **145**. 167, 1872; K. S. Nargund and H. E. Watson, *Journ. Indian Inst. Science*, **7**. 149, 1926.

[10] G. A. Barbieri and F. Lanzoni, *Atti Accad. Lincei*, (5), **20**. i, 161, 1911; B. Reinitzer, *Zeit. angew. Chem.*, **26**. 456, 1913.

[11] J. Schulze, *Zeit. anorg. Chem.*, **10**. 148, 1895; G. Krüss, *ib.*, **8**. 454, 1895; G. Krüss and O. Unger, *ib.*, **8**. 45, 1895; S. H. C. Briggs, *ib.*, **56**. 246, 1908; C. O. Weber, *Dingler's Journ.*, **279**. 284, 1891; N. Parravano and A. Pasta, *Gazz. Chim. Ital.*, **37**. ii, 252, 1907; M. Gröger, *Zeit. anorg. Chem.*, **66**. 7, 1910.

[12] A. J. Cox, *Zeit. anorg. Chem.*, **40**. 155, 1904; **50**. 242, 1906; *Ueber basische Quecksilbersalze*, Leipzig, 1904; *Journ. Amer. Chem. Soc.*, **28**. 1694, 1906; J. A. Atanasiu, *Journ. Chim. Phys.*, **23**. 501, 1926; C. Hensgen, *Rec. Trav. Chim. Pays. Bas.*, **5**. 187, 1886; C. H. Hirzel, *Liebig's Ann.*, **84**. 258, 1852; *Ueber die Einwirkungen des Quecksilbers auf des Ammoniak und die Ammoniaksalze*, Leipzig, 1852; S. H. C. Briggs, *Zeit. anorg. Chem.*, **56**. 246, 1908; K. A. Hofmann, *Ber.*, **49**. 1650, 1916; A. Gawalowsky, *Pharm. Post.*, **39**. 602, 1906.

[13] R. E. Meyer, *Das Indium*, Leipzig, 1868; G. Calcagni, *Gazz. Chim. Ital.*, **55**. 396, 1925.

[14] W. Crookes, *Chem. News*, **8**. 255, 1863; M. Hebberling, *Liebig's Ann.*, **134**. 11, 1865; L. Schulerud, *Journ. prakt. Chem.*, (2), **19**. 39, 1879; E. Carstanjen, *ib.*, (1), **102**. 65, 129, 1867; J. E. Willm, *Ann. Chim. Phys.*, (4), **5**. 59, 1865; *Bull. Soc. Chim.*, (2), **2**. 89, 1864; F. J. Faktor, *Pharm. Post*, **38**. 219, 1905.

[15] A. J. Cox, *Zeit. anorg. Chem.*, **40**. 155, 1904; **50**. 242, 1906; *Ueber basische Quecksilbersalze*, Leipzig, 1904; *Journ. Amer. Chem. Soc.*, **28**. 1694, 1906; W. Borchers, *Zeit. Elektrochem.*, **3**. 484, 1897; K. Elbs and R. Nübling, *ib.*, **9**. 780, 1903; K. Preis and B. Rayman, *Ber.*, **13**. 343, 1880; O. Mayer, *ib.*, **36**. 1743, 1903; W. Autenrieth, *ib.*, **35**. 2063, 1902; C. Lückow, *German Pat.*, *D.R.P.* 91707, 1894; 105143, 1895; *Brit. Pat. No.* 14801, 1895; E. Hatschek, *Koll. Zeit.*, **14**. 115, 1914; V. Moravek, *ib.*, **49**. 39, 1929; J. Milbauer, *Chem. Listy*, **20**. 389, 1926.

[16] A. J. Cox, *Journ. Amer. Chem. Soc.*, **28**. 1694, 1906; *Ueber basische Quecksilbersalze*, 1904; *Zeit. anorg. Chem.*, **50**. 226, 1906; K. Preis and B. Rayman, *Sitzber. Böhm. Ges.*, 507, 1879.

[17] P. Pfeiffer, *Zeit. anorg. Chem.*, **24**. 297, 1900; E. Wilke-Dörfurt and H. G. Mureck, *ib.*, **184**. 121, 1929; E. Wilke-Dörfurt and K. Niederer, *ib.*, **184**. 145, 1929; W. J. Sell, *Proc. Roy. Soc.*, **33**. 267, 1882; **45**. 321, 1889; O. T. Christensen, *Journ. prakt. Chem.*, (2), **24**. 86, 1881; G. Calcagni, *Gazz. Chim. Ital.*, **55**. 396, 1925; A. Werner and J. von Halban, *Ber.*, **39**. 2670, 1906.

[18] M. Gröger, *Zeit. anorg. Chem.*, **66**. 7, 1910; S. H. C. Briggs, *ib.*, **56**. 246, 1908; N. Parravano and A. Pasta, *Gazz. Chim. Ital.*, **37**. ii, 252, 1907; S. Husain and J. R. Partington, *Chem. News*, **133**. 386, 1926; G. Calcagni, *Gazz. Chim. Ital.*, **55**. 396, 1925; E. Wilke-Dörfurt and H. G. Mureck, *Zeit. anorg. Chem.*, **184**. 121, 1929.

[19] J. Schulze, *Zeit. anorg. Chem.*, **10**. 154, 1895; A. Werner and K. Dawe, *Ber.*, **40**. 797, 1907; A. Werner, *ib.*, **41**. 3010, 1908; A. Werner and A. R. Klein, *Zeit. anorg. Chem.*, **14**. 39, 1897; S. M. Jörgensen, *ib.*, **5**. 167, 1894; *Journ. prakt. Chem.*, (2), **18**. 234, 1878; (2), **23**. 247, 1881; G. Krüss and O. Unger, *Zeit. anorg. Chem.*, **8**. 452, 1895; O. W. Gibbs, *Amer. Journ. Science*, (2), **37**. 57, 1864; *Proc. Amer. Acad.*, **10**. 8, 1875; **11**. 28, 1876; G. Vortmann, *Monatsh.*, **6**. 441, 1885; *Ber.*, **15**. 1895, 1882; A. Werner and A. A. Wolberg, *ib.*, **38**. 997, 1905; P. Ray and P. V. Sarkar, *Journ. Indian Chem. Soc.*, **1**. 289, 1925; S. H. C. Briggs, *Journ. Chem. Soc.*, **115**. 67, 1919; 685, 1929.

[20] S. H. C. Briggs, *Zeit. anorg. Chem.*, **56**. 246, 1908; G. Chiavarino, *Riv. Min. Crist. Ital.*, **48**. 82, 1917.

[21] G. B. Buckton, *Journ. Chem. Soc.*, **5**. 213, 1852; S. G. Hedin, *Om pyridinens platinabaser* Lund, 1885; P. T. Cleve, *Acta Univ. Upsala*, **6**. 61, 1866; *Svenska Akad. Handl.*, **7**. 13, 1868; O. Carlgren and P. T. Cleve, *Oefvers. Akad. Förh.*, **47**. 305, 1890; *Zeit. anorg. Chem.*, **1**. 74, 1892.

§ 17. The Trichromates

M. Siewert[1] evaporated a soln. of ammonium dichromate in nitric acid, and obtained **ammonium trichromate,** $(NH_4)_2Cr_3O_{10}$. E. Jäger and G. Krüss recommended nitric acid of sp. gr. 1·39; but added that it is more convenient to prepare the salt from a soln. of ammonium dichromate in a conc. soln. of chromic acid. F. A. H. Schreinemakers studied the conditions of equilibrium, and his results are summarized in Fig. 29. The dark garnet-red, rhombic bipyramids were found by G. N. Wyrouboff to have the axial ratios $a:b:c=0{\cdot}8446:1:0{\cdot}8344$; the (100)-cleavage is distinct. The optic axial angle $2E=44°\ 30'$; and the optical character is positive. E. Jäger and G. Krüss gave 2·329 at 10°, and 2·342 at 13° for the sp. gr. M. Siewert said that the salt darkens at 110°–120°, and E. Jäger and G. Krüss said that the darkening which appears at 160°–170° is a sign of decomposition which begins at about 150°. Detonation occurs at about 190°. The residue is chromic oxide, or, according to M. Siewert, chromic oxide mixed with chromium trioxide. Water, nitrogen and nitrogen oxides—*e.g.* NO_2—are evolved. W. C. Ball said that the thermal decomposition resembles that with the dichromate (*q.v.*). The salt does not deliquesce, but it slowly decomposes in moist air forming chromic acid and ammonium dichromate; similarly also in contact with water.

F. A. H. Schreinemakers[2] did not find **lithium trichromate,** $Li_2Cr_3O_{10}$ in his study of the ternary system Li_2O–CrO_3–H_2O at 30°—Fig. 31. A. Stanley prepared dark red deliquescent crystals of **sodium trichromate,** $Na_2Cr_3O_{10}.H_2O$, by evaporating over sulphuric acid a soln. of sodium dichromate in chromic acid. The conditions of equilibrium, worked out by F. A. H. Schreinemakers, are summarized in Fig. 32. The crystals effloresce over sulphuric acid. The deliquescent crystals are soluble in water without decomposition even at 100°; and F. A. H. Schreinemakers found that at 30° a sat. soln. contains 70 per cent. $Na_2Cr_3O_{10}$. F. Mylius and R. Funk found that a soln. sat. at 18° contains 80·60 per cent. of salt and has a sp. gr. 2·059; and they gave for the percentage solubility at 0°, 15°, 55°, and 99°, respectively 80·03, 80·44, 82·68, and 85·78.

E. Mitscherlich[3] prepared **potassium trichromate,** $K_2Cr_3O_{10}$, from a soln. of potassium dichromate and nitric acid; F. Bothe recommended working with nitric acid of sp. gr. 1·210, and at 60°; E. Jäger and G. Krüss used nitric acid of sp. gr. 1·19. C. Schmidt used conc. nitric acid, but G. N. Wyrouboff said that if the nitric acid be too conc.—over 1·41 sp. gr.—some tetrachromate is formed. H. Reinsch, and C. J. B. Karsten observed the tendency of potassium nitrate to crystallize out with the trichromate in nitric acid soln.; and L. Darmstädter mistook the impure product for nitrochromate. M. Siewert separated the product from potassium nitrate by fractional crystallization. C. von Hauer, M. Siewert, and E. Jäger and G. Krüss obtained the trichromate by evaporating over sulphuric acid a soln. of potassium dichromate in chromic acid; F. A. H. Schreinemakers, and I. Koppel and E. Blumenthal studied the conditions of equilibrium, and the results are summarized in Figs. 36 to 41. Potassium trichromate furnishes deep red, prismatic crystals; and F. Bothe reported that the monoclinic prisms have the axial ratios $a:b:c=0{\cdot}8437:1:0{\cdot}8318$, and $\beta=101°\,0'$; the (010)-cleavage is distinct. F. Bothe gave 3·613 for the sp. gr.; H. G. F. Schröder, 2·676–2·702; L. Playfair and J. P. Joule, 2·655; and E. Jäger and G. Krüss, 2·667 at 10°—crystallized from chromic acid—and 2·648 at 11°—crystallized from nitric acid. The hardness is 2·5. I. Traube found the drop-weight of the molten trichromate to be 231 mgrms. F. Bothe said that the salt decrepitates a little when heated, and melts at 145°–150°; E. Jäger and G. Krüss said that the trichromate blackens at 220°, and melts at 250°. E. Groschuff said that the salt decomposes when melting. M. Berthelot gave for the heat of formation in the solid state: $(K_2CrO_4,2CrO_3)=14{\cdot}1$ Cals.; and T. Graham gave for the heat of soln., $-14{\cdot}2$ Cals. On exposure to air, the crystals lose their lustre and become opaque. The salt is freely soluble in water and there is a small fall in temp., and the trichromate decomposes into dichromate and chromic acid. P. Walden also inferred from the electrical conductivity, μ mho of the aq. soln. of a mol of the salt in v litres of water at 25°, *viz.*

v . .	32	64	128	256	512	1024
μ . .	275·9	282·9	286·1	286·4	283·4	278·2

that the salt is partially decomposed. L. A. Welo studied the magnetic susceptibility. F. Bothe found that the trichromate is soluble in alcohol, and the alcoholic soln. rapidly decomposes in light. A. Naumann found that the salt is soluble in acetone. G. N. Wyrouboff studied solid soln. of potassium and ammonium trichromates, and saw that the hexagonal crystals have the axial ratio $a:c=1:1{\cdot}0844$ with 58·5 to 69·7 per cent. of the ammonium salt.

F. A. H. Schreinemakers and H. Filippo[4] showed the conditions of equilibrium, Fig. 46, for **rubidium trichromate,** $Rb_2Cr_3O_{10}$, in soln. of chromic acid; and F. A. H. Schreinemakers and D. J. Meijeringh, the conditions of equilibrium, Fig. 47, of **cæsium trichromate,** $Cs_2Cr_3O_{10}$. The dark red, trigonal crystals were stated by F. R. Fraprie to have the axial ratio $a:c=1:1·5549$ and not to be isomorphous with the other trichromates.

M. Gröger[5] could not prepare **copper trichromate,** $CuCr_3O_{10}$. H. von Foullon passed carbon dioxide into a soln. of calcium chromate and obtained a precipitate corresponding with **calcium oxytrichromate,** $CaO.CaCr_3O_{10}$. K. Preis and B. Rayman prepared garnet-red deliquescent crystals of **strontium trichromate,** $SrCr_3O_{10}.3H_2O$, by the method employed in preparing the dichromate, but using a large excess of chromic acid. J. F. Bahr prepared **potassium barium trichromate,** $K_2Cr_3O_{10}.2BaCr_3O_{10}.3H_2O$, from a chromic acid soln. of barium and potassium dichromates. The reddish-brown needles are very deliquescent, and are decomposed by water.

M. Gröger[6] prepared dark red, deliquescent crystals of **zinc trichromate,** $ZnCr_3O_{10}.3H_2O$, by evaporating in vacuo a soln. of zinc dichromate in chromic acid. He also obtained **cadmium trichromate,** $CdCr_3O_{10}.H_2O$, in dark reddish-brown crystals by an analogous process. A. Gawalowsky obtained pale red crystals of *mercuric polychromate* by the action of an acidified soln. of potassium dichromate on mercury.

W. Crookes[7] obtained **thallous trichromate,** $Tl_2Cr_3O_{10}$, by digesting the chromate with sulphuric acid; and J. E. Willm, by digesting the dichromate with nitric acid. The red, crystalline powder behaves like the monochromate towards aq. and alcoholic hydrochloric acid. 100 grms. of water at 15° dissolve 0·0355 grm. of the trichromate, and at 100°, 0·2283 grm.

References.

[1] M. Siewert, *Zeit. ges. Naturwiss.*, **19**. 22, 1862; E. Jäger and G. Krüss, *Ber.*, **22**. 2034, 1889; F. A. H. Schreinemakers, *Chem. Weekbl.*, **1**. 395, 1905; *Zeit. phys. Chem.*, **55**. 94, 1906; G. N. Wyrouboff, *Bull. Soc. Min.*, **3**. 145, 1880; W. C. Ball, *Journ. Chem. Soc.*, **95**. 87, 1909.

[2] A. Stanley, *Chem. News*, **54**. 196, 1886; F. A. H. Schreinemakers, *Chem. Weekbl.*, **2**. 211, 1905; *Zeit. phys. Chem.*, **55**. 94, 1906; F. Mylius and R. Funk, *Ber.*, **33**. 3688, 1900.

[3] T. Graham, *Mem. Chem. Soc.*, **1**. 82, 1842; *Phil. Mag.*, (3), **20**. 539, 1842; F. Bothe, *Journ. prakt. Chem.*, (1), **46**. 184, 1849; H. Reinsch, *ib.*, (1), **28**. 371, 1843; C. von Hauer, *ib.*, (1), **103**. 118, 1868; *Sitzber. Akad. Wien*, **39**. 439, 1860; **53**. 221, 1866; I. Koppel and E. Blumenthal, *Zeit. anorg. Chem.*, **53**. 263, 1907; E. Groschuff, *ib.*, **58**. 102, 1908; F. A. H. Schreinemakers, *Chem. Weekbl.*, **1**. 837, 1905; *Zeit. phys. Chem.*, **55**. 71, 1906; J. W. Retgers, *ib.*, **2**. 70, 1888; E. Jäger and G. Krüss, *Ber.*, **22**. 2039, 1889; C. Schmidt, *ib.*, **25**. 2917, 1892; L. Darmstädter, *ib.*, **4**. 117, 1871; I. Traube, *ib.*, **24**. 3077, 1891; A. Naumann, *ib.*, **37**. 4328, 1904; M. Siewert, *Zeit. ges. Naturwiss.*, **19**. 15, 1862; L. A. Welo, *Phil. Mag.*, (7), **6**. 481, 1928; H. G. F. Schröder, *Liebig's Ann.*, **174**. 249, 1874; C. J. B. Karsten, *Philosophie der Chemie*, Berlin, 167, 1843; E. Mitscherlich, *Lehrbuch der Chemie*, Berlin, **2**. 759, 1844; G. N. Wyrouboff, *Bull. Soc. Min.*, **3**. 136, 1880; **4**. 25, 120, 1881; L. Playfair and J. P. Joule, *Mem. Chem. Soc.*, **2**. 450, 1843; M. Berthelot, *Thermochimie*, Paris, **1**. 282, 1897; *Ann. Chim. Phys.*, (5), **17**. 133, 1879; P. Walden, *Zeit. phys. Chem.*, **1**. 520, 1887; **2**. 70, 1888.

[4] F. A. H. Schreinemakers and H. Filippo, *Chem. Weekbl.*, **3**. 157, 1906; F. A. H. Schreinemakers and D. J. Meijeringh, *ib.*, **5**. 811, 1908; F. R. Fraprie, *Amer. Journ. Science*, (4), **21**. 309, 1906.

[5] H. von Foullon, *Jahrb. geol. Reichsanst. Wien*, **40**. 421, 1890; K. Preis and B. Rayman, *Ber.*, **13**. 342, 1880; M. Gröger, *Zeit. anorg. Chem.*, **66**. 7, 1910; J. F. Bahr, *Oefvers. Akad. Förh.*, **9**. 155, 1852; *Journ. prakt. Chem.*, (1), **60**. 60, 1853.

[6] M. Gröger, *Zeit. anorg. Chem.*, **58**. 417, 1908; *Sitzber. Akad. Wien*, **113**. 162, 1904; A. Gawalowsky, *Pharm. Post*, **39**. 602, 1906.

[7] W. Crookes, *Chem. News*, **8**. 255, 1863; J. E. Willm, *Ann. Chim. Phys.*, (4), **5**. 59, 1865; *Bull. Soc. Chim.*, (2), **2**. 89, 1864.

§ 18. The Tetrachromates

G. N. Wyrouboff[1] reported **ammonium tetrachromate,** $(NH_4)_2Cr_4O_{13}$, to be formed by crystallization from a soln. of ammonium dichromate in hot nitric acid of sp. gr. 1·41. E. Jäger and G. Krüss could not obtain the salt in this way, but they obtained it by slowly cooling a soln. of the trichromate in nitric acid of sp. gr. 1·39. F. A. H. Schreinemakers studied the conditions of equilibrium, and the results are summarized in Fig. 29. The brownish-red, crystalline aggregates are less stable than the lower chromates. E. Jäger and G. Krüss observed that the salt is hygroscopic, and is decomposed by moisture into the dichromate and chromic acid. The crystalline salt is stable in a dry atmosphere. It blackens when heated to 160°, melts at 170°, and decomposes suddenly at 175°, giving off nitric oxide, etc., and leaving a mixture of chromic oxide and chromium trioxide. J. J. Pohl reported crystals of *ammonium tetrachromate*, thought to be $(NH_4)_{10}Cr_4O_{17}$, in the preparation of the normal tetrachromate. J. Schabus found the monoclinic crystals had the axial ratios $a : b : c = 0·7458 : 1 : 0·4955$, and $\beta = 106° 51'$.

F. A. H. Schreinemakers could not prepare **lithium tetrachromate,** $Li_2Cr_4O_{13}$; but he showed that **sodium tetrachromate,** $Na_2Cr_4O_{13}.H_2O$, can exist under the conditions indicated in Fig. 34. F. Mylius and R. Funk prepared this salt by evaporating a soln. of sodium chromate in an excess of chromic acid. The garnet-red, deliquescent plates melt at 40°–50° with the separation of chromium trioxide. The salt dissolves in water without decomposition. A sat. soln. at 18° has 74·60 per cent. of $Na_2Cr_4O_{13}$, and has a sp. gr. of 1·926; and at 0°, 16°, and 22°, the respective percentage solubilities are 72·19, 74·19, and 76·01.

M. Siewert prepared potassium tetrachromate, $K_2Cr_4O_{13}$, by evaporating a soln. of potassium trichromate in conc. nitric acid slowly on a sand-bath, and cooling the mixture. The crystalline plates have the colour of mercuric iodide, and are freed from nitric acid by press. on porous titles, and by drying at 140°. E. Jäger and G. Krüss, and G. N. Wyrouboff used nitric acid of sp. gr. 1·4; and C. Schmidt, acid of sp. gr. 1·48–1·52. The contamination of the salt with nitrate led L. Darmstädter to regard it as a nitrochromate. E. Jäger and G. Krüss, and G. N. Wyrouboff obtained it by crystallization from a soln. of the trichromate in aq. chromic acid. F. A. H. Schreinemakers, and I. Koppel and E. Blumenthal studied the conditions of equilibrium, and the results are summarized in Figs. 36 to 41. H. Schwarz found that a soln. of a mol of potassium dichromate and 2 mols of sulphuric acid, first deposits crystals of the dichromate, and afterwards a mixture of potassium tetrachromate and sulphate. Potassium tetrachromate forms brownish-red or carmine-red, 8-sided plates and prisms, which are monoclinic; G. N. Wyrouboff gave for the axial ratios $a : b : c = 0·797 : 1 : 1·110$, and $\beta = 91° 42'$. The deliquescent crystals are stable in air; and E. Jäger and G. Krüss said that their sp. gr. is 2·649 at 11°; and that they melt at 215°; they are decomposed by water into trichromate and chromic acid.

F. Mylius and J. von Wrochem obtained dark red crystals of **calcium tetrachromate,** $CaCr_4O_{13}.6H_2O$, by evaporating over sulphuric acid a soln. of calcium carbonate in an excess of chromic acid. The salt is soluble in water.

C. F. Rammelsberg found that a soln. of chromic acid free from sulphuric acid, and half saturated with ammonia furnished a brownish-yellow salt—thought to be *ammonium hexachromate*. It decomposed with incandescence when heated. E. Jäger and G. Krüss could obtain only the dichromate by this process; and they were unable to isolate a more complex salt than the tetrachromate. This agrees with F. A. H. Schreinemaker's observations—Fig. 29.

REFERENCES.

[1] F. A. H. Schreinemakers, *Zeit. phys. Chem.*, **55**. 82, 1906; *Chem. Weekbl.*, **1**. 395, 837, 1904; **2**. 211, 1905; F. A. H. Schreinemakers and H. Filippo, *ib.*, **3**. 157, 1906; F. A. H. Schreinemakers and D. J. Meijeringh, *ib.*, **5**. 811, 1908; F. Mylius and R. Funk, *Ber.*, **33**. 3686, 1900; F. Mylius and J. von Wrochem, *ib.*, **33**. 3690, 1900; C. Schmidt, *ib.*, **25**. 2917, 1892; L. Darmstädter, *ib.*, **4**. 117, 1871; E. Jäger and G. Krüss, *ib.*, **22**. 2036, 1889; G. N. Wyrouboff, *Bull. Soc. Min.*, **4**, 17, 1881; *Bull. Soc. Chim.*, (2), **35**. 162, 1881; I. Koppel and E. Blumenthal, *Zeit. anorg. Chem.*, **53**. 228, 1906; J. Schabus, *Bestimmung der Krystallgestalten, in chemishen Laboratorien erzeugter Produkte*, Wien, 185, 1855; H. Schwarz, *Dingler's Journ.*, **186**. 31, 1867; M. Siewert, *Zeit. ges. Naturwiss.*, **19**. 15, 1862; C. F. Rammelsberg, *Pogg. Ann.*, **94**. 516, 1855; J. J. Pohl, *Journ. prakt. Chem.*, (1), **56**. 63, 1851.

§ 19. Perchromic Acid and the Perchromates

In 1847, L. C. A. Barreswil,[1] in his memoir : *Sur un nouveau composé oxygèné du chrome,* described how a deep blue soln. is produced when a conc. soln. of chromic acid is mixed with hydrogen dioxide. The soln. immediately begins to decompose with the evolution of oxygen, and this decomposition occurs more quickly with conc. soln. and with vigorous agitation. If sulphuric acid be mixed with potassium dichromate, and treated with hydrogen dioxide, oxygen is evolved and a soln. of chromic sulphate is formed. If ether be shaken up with the blue soln., the aq. layer is decolorized, and the ethereal liquor retains the blue product. The ethereal soln. is more stable than the aq. soln. If the ethereal soln. be evaporated, a conc. is attained at which the liquor suddenly decomposes with the evolution of oxygen and the formation of chromic acid. It is assumed that the blue soln. contained a perchromic acid CrO_{3+n} formed in accord with $2CrO_3+2nH_2O_2 \rightarrow 2CrO_{3+n}+2nH_2O$; and that the decomposition progresses $2CrO_{3+n} \rightarrow Cr_2O_3+(2n+3)O$, or $CrO_{3+n} \rightarrow CrO_3+nO$. F. H. Storer said that the blue coloration is so sensitive that it enables one part of potassium dichromate to be detected in 30,000 to 40,000 parts of water. G. Werther said that the presence of 0·0001 part of vanadate will mask the effect with 0·0001 part of chromate ; and C. Reichard noted that the disturbing effect of the molybdate and tungstate is not so great as that of the vanadate. C. Reichard observed that the presence of sodium hydrophosphate or hydroarsenate removes the injurious effect of vanadium.

W. M. Grosvenor found that the blue compound is also soluble in ethyl acetate or valerate, amyl chloride, amyl alcohol, and in amyl formate, acetate, butyrate, or valerate. The blue substance is not dissolved by carbon disulphide, benzene, light petroleum, toluene, nitrobenzene, aniline, paraffin and turpentine, carbon tetrachloride, chloroform, castor oil, bergamot oil, and oil of wintergreen. The soln. in ethyl acetate is said to be the most stable, but even that decomposes in about 23 hrs. G. Griggi said that the soln. in amyl alcohol is more stable than in ordinary ether, but W. M. Grosvenor did not agree. According to L. C. A. Barreswil, alkaloids—quinine, strychnine, etc.—in ethereal soln. form dirty violet precipitates insoluble in ether ; and when the precipitate is dried and treated with an acid, and ether, the blue soln. is again formed.

H. Aschoff found that the blue soln. is decolorized by ferrous salts; and, according to W. P. Jorissen and L. T. Reicher, by oxalic acid. With an excess of alkali-lye, L. C. A. Barreswil observed that oxygen is evolved and alkali chromate is formed. H. Aschoff found that lead oxide behaves like the alkali. C. F. Schönbein made some observations on the action of alkali on the blue soln. H. Aschoff found that if a dil. soln. of potassium hydroxide be added to the soln. until the ethereal layer is pale blue, water now colours the neutral aq. layer brownish-violet. The addition of more alkali results in the evolution of oxygen, and the formation of yellow alkali chromate. It is therefore inferred that the soln. of the free perchromic acid is blue, and that the salts are violet. In general, as shown by M. Martinon, acids decomposed the blue substance into salts of chromic oxide and oxygen, while alkalies form chromates.

M. Berthelot showed that with strong acids and a soln. of dichromate, hydrogen dioxide gives the blue colour of the hypothetical perchromic acid ; with the weaker acetic or phosphoric acid, the colour is violet not blue—due, it is suggested, to the formation of a brown substance along with the perchromic acid ; and with still weaker boric or hydrocyanic acid, the colour is brown and the rate of decomposition is slow. With a moderately conc. soln. of chromic acid, the liquid is first blue, then violet, brown, or even green ; but with dil. soln., at 10°, only traces of the blue perchromic acid are formed. The brown substance is the chief product. The action is most regular with an aq. soln. of a mol. of potassium dichromate per 16 litres, and an eq. quantity of a soln. containing a mol of hydrogen dioxide per 2 litres. The liquid first darkens in colour, rapidly becoming deep brown, and oxygen is liberated with effervescence, and during the reaction the liquid contains only traces of perchromic acid. The liquid then becomes clear and acquires its original colour—it contains neither hydrogen dioxide nor reduced chromic oxide. The same quantity of potassium dichromate will decompose an unlimited quantity of hydrogen dioxide. The brown intermediate product is probably a compound of hydrogen peroxide with chromic oxide: it decomposes rapidly, with regeneration of chromic acid, liberation of oxygen, and formation of water. As the thermal measurements show, the heat liberated by the reaction is identical with that liberated by the decomposition of hydrogen peroxide.

The brown colour of the unstable intermediate product points to the formation of chromium chromate. The hydrogen dioxide oxidizes the chromium chromate forming chromic acid and water. All this characterizes a catalytic reaction. Attempts by E. H. Riesenfeld, and E. Spitalsky to work out a detailed explanation of the catalyzed reaction have not been successful. When a large excess of hydrogen dioxide is present, the rate of decomposition is approximately proportional to the conc. of the chromic acid. If C_1 denotes the conc. in mols of K_2CrO_4 per litre, and k_1 the velocity constant,

C_1	0·001674	0·003132	0·02205	0·0313	0·05105	0·0674	0·1020
k_1 (obs.)	0	6·7	14·4	15·9	23·5	29·4	46·0
k_1 (calc.)	0·8	1·4	10·1	14·4	23·5	31·0	46·8

The reaction with dichromate is faster than with monochromate; and if C_2 denotes the conc. in mols of $K_2Cr_2O_7$ per litre, and k_2, the velocity constant of a first order reaction,

$C_2 \times 10^4$	0·3	1·2	2·4	4·8	7·83	9·6	45·4	90·8
k_2 (obs.)	4·5	17·2	33·7	65·3	100	123	394	829
k_2 (calc.)	4·1	16·4	32·0	65·8	108	123	394	829

The calculated values from $C_2 = 9{\cdot}6 \times 10^{-4}$ are no longer in accord with the observed. With dichromate alone, or in feebly acidic soln., some of the dichromate is reduced to a tervalent chromic salt; the proportion reduced depends on the acidity, *i.e.* on the H$^{\cdot}$-ion conc.; thus, with soln. containing 0·00546 mol Cr per litre at 25°, the percentage proportions of tervalent chromium are:

[H$^{\cdot}$]	0	0·00182	0·00354	0·00547	0·00783	0·00818	0·01089
Cr$^{\cdots}$	2·0	8·7	18·9	28·5	36·2	43·6	57·5 per cent.

These are equilibrium values in the sense that if a mixture contains more than this proportion of Cr$^{\cdots}$, oxidation to chromate occurs. E. Spitalsky found that when hydrogen dioxide is present in considerable excess, the rate at which it is decomposed is nearly independent of its conc., being approximately proportional to the cube root of the dioxide conc., but when the dioxide conc. has diminished to such an extent that the ratio $H_2O_2 : CrO_3$ is not more than 10 : 1, the velocity suddenly rises to two or three times its former value and then falls rapidly to zero, the dioxide being completely decomposed. The decomposition is relatively less rapid the greater the initial dioxide conc. for a definite conc. of chromic acid. When the dioxide is present in considerable excess, the rate of decomposition is approximately proportional to the chromic acid conc. The reaction velocity at any instant is completely determined by the dioxide and chromic acid conc. at that instant—for example, the sharp maximum in the velocity curve occurs at the same dioxide conc. for a definite chromic acid conc., independent of the initial conc. of the dioxide. E. H. Riesenfeld inferred that the H_3CrO_8-acid is first formed by the consumption of H$^{\cdot}$-ions; and as the acidity of the soln. is reduced, H_3CrO_7-acid appears. This is in harmony with E. Spitalsky's observation that a definite proportion of the chromic acid catalyst is reduced to a tervalent chromium salt. E. I. Orloff also discussed these complex reactions; and G. N. Ridley reviewed the general properties of perchromic acid.

H. Moissan said that the blue compound cannot be formed by the action of ozone, on a soln. of chromic acid, although A. Mailfert said that perchromic acid is formed if ether be also present. H. Moissan added that the blue perchromic acid is produced by the electrolysis of soln. of chromic acid only when hydrogen dioxide is first formed. E. H. Riesenfeld found that when a soln. of 16·6 grms. of chromic acid in 100 c.c. of a 30-per cent. soln. of sulphuric acid is electrolyzed, using platinum electrodes, and a porous cathode cell cooled by means of ether and carbon dioxide, a higher oxidation product of chromium, which can be detected by precipitation with ammonia, is probably formed, but decomposes as the conc. increases until the velocity of formation becomes equal to that of decomposition. Since chromic oxide, Cr_2O_3, and not chromic acid, is formed by the decomposition, the quantity of oxygen lost is greater than that produced by the electrolysis.

Two methods have been employed for finding the nature of the blue product: (i) By isolating the substance, its salts or their equivalent; and (ii) By determining the oxidizing power or the amount of oxygen set free during its decomposition. L. C. A. Barreswil found that when an acidified soln. of potassium dichromate is treated with hydrogen dioxide, 4 mols of oxygen are given off per mol of $K_2Cr_2O_7$; and he assumed that the perchromic acid, $Cr_2O_7.H_2O$, is formed as an intermediate compound. H. Aschoff represented the reaction: $2CrO_3+H_2O_2=H_2O+Cr_2O_7$ followed by $Cr_2O_7+4H_2O_2\rightarrow Cr_2O_3+4H_2O+4O_2$. B. C. Brodie found that with an excess of chromic acid, 6 gram-atoms of oxygen are evolved per 2 mols of CrO_3; and with an excess of hydrogen dioxide, 9 gram-atoms of oxygen; while T. Fairley's observations led him to assume that the intermediate perchromic acid is $CrO_6.3H_2O$. M. Martinon found that the maximum depth of blue coloration is developed when 2 mols. of CrO_3 and 4 mols. of H_2O_2 are present, and hence he regarded the perchromic acid as $4H_2O_2.2CrO_3$, *i.e.* H_4CrO_7, with the anhydride CrO_5. A. Carnot found that chromic acid is quantitatively reduced by hydrogen dioxide, and M. Berthelot observed that the amount of oxygen developed depends on whether the hydrogen dioxide is poured into the chromic acid or conversely. In the first case the result agrees with: $2CrO_3+3H_2O_2+3H_2SO_4=Cr_2(SO_4)_3+3O_2+6H_2O$, *i.e.* the chromic acid and hydrogen dioxide each lose the same quantity of oxygen. In the second case, the reaction seems to occur in two stages, $2CrO_3+H_2O_2=Cr_2O_7+H_2O$, and then $Cr_2O_7+4H_2O_2=Cr_2O_3+4H_2O+4O_2$ when 1·66 times as much oxygen is derived from the hydrogen dioxide as from the chromium trioxide. The intermediate Cr_2O_7 is considered to be the anhydride of the blue perchromic acid. E. Baumann confirmed M. Berthelot's conclusions; and observations were also made by A. Bach, and L. Marchlewsky. E. H. Riesenfeld represented the reaction between hydrogen dioxide and an excess of chromic acid by the equation: $2CrO_3+3H_2O_2=Cr_2O_3+3H_2O+3O_2$ with the intermediate formation of a Cr_2O_9-oxide: $2CrO_3+3H_2O_2=Cr_2O_9+3H_2O$ followed by $Cr_2O_9=Cr_2O_3+3O_2$; and with the hydrogen dioxide in excess, $2CrO_3+2H_2O_2=2CrO_4+2H_2O$ followed by $2CrO_4+5H_2O_2=Cr_2O_3+5H_2O+5O_2$, or else according to $2CrO_3+7H_2O_2=Cr_2O_{13}+7H_2O$ followed by $Cr_2O_{13}=Cr_2O_3+5O_2$. H. E. Patten argued that it is the hydrogen not the chromium which forms a higher peroxide. He said:

> When a sat. soln. of potassium dichromate is cooled to $-16°$ and treated with 2 per cent. soln. of hydrogen dioxide at the same temp., a white, solid substance separates and the soln. turns blue. If a cold sat. soln. of sodium acetate is added to this soln., it assumes the lake-colour of chromous acetate, and if left for half an hour the green colour of chromic acetate appears. Solid chromous acetate may be obtained by extracting the blue soln. with ether and adding sodium acetate to the blue ethereal soln. The electrical conductivity of the blue ethereal soln. of "chromous oxide" is less than 2×10^{-8} at 0°. The simplest explanation of these facts is said to be that chromic acid is reduced to the chromous state by hydrogen dioxide, and a higher oxide of hydrogen is produced.

This hypothesis, said K. A. Hofmann and H. Hiendlmaier, is untenable because much oxygen is evolved when hydrogen dioxide is mixed with chromic acid, and chromous salts are rapidly oxidized even by air, and they decompose water.

E. H. Riesenfeld pointed out that in the observations just indicated it is assumed that only one chemical individual is concerned in the reaction when either the hydrogen dioxide or the chromic acid is in excess. Actually, several products are probably produced, and these are all prone to decomposition. Hence, the term **perchromic acid** applied to the blue product does not necessarily refer to a chemical individual. H. Moissan tried to isolate the blue compound by evaporating the ethereal soln. at −20°; he obtained a deep indigo-blue, oily, liquid with a composition corresponding with $CrO_3.H_2O_2$. E. Péchard added baryta-water to a well-cooled soln. of chromic acid containing an excess of hydrogen dioxide and obtained a brown precipitate approximating $BaCrO_5$, but which O. Wiede regarded as a mixture of barium chromate and dioxide. C. Häussermann treated a mush of chromium hydroxide and water with sodium dioxide at 10°-20°, and obtained reddish-brown, efflorescent crystals, $Na_6Cr_2O_{15}.28H_2O$. The subsequent observations of O. Wiede, E. H. Riesenfeld and co-workers, and K. A. Hofmann and H. Hiendlmaier have shown that the following derivatives of the oxidation products of chromic acid can be recognized:

Compounds of the type: R_3CrO_8, or the red perchromates or **triperchromates.**—E. H. Riesenfeld and co-workers discovered that these compounds are formed when an alkaline soln. of chromic acid is treated with 30 per cent. hydrogen dioxide. For example, the ammonium salt, $(NH_4)_3.CrO_8$, is prepared as follows:

A mixture of 50 c.c. of 25 per cent. ammonia, 25 c.c. of 50 per cent. chromic acid, and 75 c.c. of water is cooled until ice begins to separate; 25 c.c. of 30 per cent. hydrogen dioxide is added, drop by drop, with constant shaking and keeping the temp. below 0°. The soln. becomes at first reddish-yellow, and then brownish-black, and in one or two hours, crystals of the ammonium salt separate out. These are washed with 95 per cent. alcohol until the runnings show no coloration due to chromic acid. The salt is dried with ether, or on a porous tile. The sodium and potassium salts can be obtained in an analogous manner.

The preparation of **ammonium triperchromate,** $(NH_4O.O)_3CrO_2$, or $(NH_4)_3CrO_8$, or *red ammonium perchromate,* has just been described. E. H. Riesenfeld and co-workers said that the salt forms reddish-brown, doubly refracting, octahedral crystals. The salt decomposes when heated to 40° forming ammonium chromate; and at 50° it explodes forming chromic oxide. It cannot be kept more than 2 days at ordinary temp. without losing oxygen. Percussion, or contact with sulphuric acid results in an explosion with the formation of chromic oxide dust. The salt forms a reddish-brown soln. with a little cold water, and, in the presence of a little alkali, it can be kept for a day without decomposition; when the soln. is boiled it forms oxygen and chromate, and this the more quickly, the smaller the conc. of the HO-ions. If the soln. be acidified, blue perchromic acid is formed, and this at once decomposes into oxygen and a chromic salt, without forming a chromate. The salt is insoluble in alcohol and ether, and is not attacked by the boiling liquids. Alcohol with more than 50 per cent. of water decomposes the salt at ordinary temp. with the formation of chromate and aldehyde, and in acidic soln. the chromate is reduced at the same time to a chromic salt. C. W. Balke showed that the salts are isomorphous with the corresponding pertantalates. The isomorphism between the pertantalates, percolumbates and perchromates was discussed by G. Böhm. E. H. Riesenfeld and co-workers prepared **sodium triperchromate,** Na_3CrO_8—possibly with H_2O—as previously indicated. The reddish-yellow plates are doubly refracting, and deliquescent. The salt cannot be satisfactorily dried; and it is preserved in an atm. sat. with water-vapour. It decomposes explosively at 115°. When dried, it loses oxygen and forms a yellow powder possibly NH_3HCrO_8. It is slightly soluble in cold water, and insoluble in alcohol and ether. E. H. Riesenfeld obtained in a similar manner **potassium triperchromate,** K_3CrO_8. The dark red prisms are doubly refracting and slightly pleochroic. The salt was kept for a month without decomposition; it does not decompose by percussion, and at 170°, it slowly gives off oxygen and forms the chromate. It decomposes explosively at 178°, or in contact with conc. sulphuric acid. The impure salt is explosive.

The salt is sparingly soluble in water, and insoluble in alcohol and ether. The f.p., and the electrical conductivity of the aq. soln. show that the salt is completely ionized.

(2) *Compounds of the type:* RH_2CrO_7 *or* $RCrO_5.H_2O_2$, *or the blue perchromates,* or **diperchromates.**—These compounds were discovered by O. Wiede. They are less stable than the red perchromates and are formed by the action of an alcoholic soln. of an alkali on the blue ethereal soln. of perchromic acid at —5° to —10°. K. A. Hofmann and H. Hiendlmaier obtained the compound by the action of, say, a soln. of ammonium chromate and nitrate on hydrogen dioxide; and E. H. Riesenfeld and co-workers, by the action of 30 per cent. hydrogen dioxide on an acidic soln. of a chromate—for example:

The ammonium salt, $(NH_4)H_2CrO_7$, is formed by mixing 100 c.c. of water, 5 c.c. of conc. hydrochloric acid, 10 grms. of ammonium chloride, 10 c.c. of 5 per cent. chromic acid, and 25 c.c. of 30 per cent. hydrogen dioxide. If in the preparation of the red perchromates, the mixture is treated with hydrochloric, oxalic or acetic acid, before the addition of hydrogen dioxide, the blue perchromates are formed.

O. Wiede, K. A. Hofmann and H. Hiendlmaier, and E. H. Riesenfeld and co-workers prepared **ammonium diperchromate,** $(HO.O)_2(NH_4O)CrO_2$, or $NH_4H_2CrO_7$, or *blue ammonium perchromate,* as just indicated. The bluish-black or violet crystals are pleochroic between pale reddish-brown and dark bluish-violet. If moisture be excluded, the salt can be kept some days without decomposition, but it gradually passes into ammonium dichromate. When rapidly heated, the salt burns with a hissing noise forming chromic oxide and nitrogen oxides. The salt dissolves in ice-cold water forming a violet-brown soln. which has a neutral reaction. The conc., aq. soln. rapidly decomposes with the evolution of oxygen, and the formation of ammonium dichromate; at a higher temp., the reaction proceeds more quickly still. Dil. sulphuric acid forms a blue soln. which quickly decomposes into oxygen and chromic sulphate. If a layer of ether be poured over the solid, or the ice-cold soln., and the liquid be acidified with sulphuric acid, the ether extracts the blue perchromic acid. The fixed alkalies act like water; with aq. ammonia, a gas is evolved and, with cold soln., the end-product is chromium triamminotetroxide. According to O. Wiede, the diperchromate is insoluble in alcohol, but according to E. H. Riesenfeld and co-workers, it is somewhat soluble in that menstruum. The salt is insoluble in ether, ligroin, and chloroform. Lead acetate, or barium chloride produces a violet-brown precipitate which soon gives off gas and forms the yellow chromate; silver nitrate gives a brownish-violet coloration which immediately forms reddish-brown silver chromate; ferric chloride gives a grass-green coloration which when heated, or allowed to stand, becomes yellow with the evolution of gas; with ferrous sulphate, gas is evolved and a yellow soln. is formed; copper sulphate is without action; and potassium permanganate forms a blood-red soln. which when acidified gives off oxygen, and deposits a manganese peroxide. O. Wiede, and E. H. Riesenfeld, prepared **potassium diperchromate,** KH_2CrO_7, in an analogous manner. The salt forms pleochroic prisms—red, and violet. The dark violet powder detonates a few degrees above 0°; the crystals are more stable, but they decompose at room temp. The salt dissolves in water, forming a brown soln. which, when warmed, gives off oxygen and forms potassium dichromate. Its reactions resemble those of the ammonium salt.

(3) *Compounds of the type:* $HCrO_5$ *with an organic nitrogen base,* or **monoperchromates.**—O. Wiede first prepared these compounds, which are blue or violet in colour, and assigned to them the formula $RCrO_3.H_2O_2$. E. H. Riesenfeld showed that they are to be regarded as complex salts of perchromic acid, $HCrO_5$, with an organic base—tetramethylammonium, $N(CH_3)_4CrO_5$, aniline, $HCrO_5.C_6H_5.NH_2$, pyridine, $HCrO_5.C_5H_5N$, piperidine, $HCrO_5.C_5H_{11}N$, or quinoline, $HCrO_5.C_9H_7N$. O. Wiede obtained them by the addition of the base to the blue ethereal soln. of perchromic acid cooled to 0°. E. H. Riesenfeld obtained the pyridine salt as follows:

A soln. of a gram of chromium trioxide in 100 c.c. of water is treated with 10 grms. of pyridine, and 25 c.c. of a 3 per cent. soln. of hydrogen dioxide at room temp. When the mixture is allowed to stand for a short time, blue crystals of $HCrO_5.C_5H_5N$ separate out.

O. Wiede prepared **tetramethylammonium monoperchromate,** $(CH_3)_4NCrO_5$, in violet, prismatic crystals, which form a brown soln. with water. It can be kept in the cold for some days. As previously indicated, complex salts were also prepared with aniline, pyridine, piperidine, and quinoline. The pyridine salt obtained by O. Wiede, K. A. Hofmann and H. Hiendlmaier, and E. H. Riesenfeld and co-workers furnished blue, rhombic plates, which were doubly refracting, and pleochroic. The salt is fairly stable when dry, but in moist air, it slowly decomposes forming chromic acid. It detonates with a small rise of temp., or by contact with sulphuric acid. Its general reactions are like those of the other perchromates.

(4) *Compounds of the type:* $CrO_4.3NH_3$, or **complex chromium tetroxides.**—These compounds were also discovered by O. Wiede, who also found that the 3 mols. of ammonia can be replaced by 3 mols of potassium cyanide indicating that the compound is chromium triamminotetroxide. E. H. Riesenfeld also prepared $2CrO_4.5KCy.5H_2O$, or $K_5[(CrO_4)_2(Cy)_5].5H_2O$; and K. A. Hofmann and H. Hiendlmaier, a compound with ethylene diamine, $CrO_4.C_2H_4N_2.2H_2O$, and one with hexamethylenetriamine, $CrO_4.C_6H_{12}N_4$. O. Wiede prepared the triamminotetroxide by shaking 100 c.c. of 10 per cent. hydrogen dioxide with a soln. of 10 grms. of chromium trioxide in 500 c.c. of water with 500 grms. of ether free from alcohol; and then adding 50 c.c. of cold, conc. ammonia. The precipitate which forms can be recrystallized from aq. ammonia. K. A. Hofmann and H. Hiendlmaier obtained it by the action of hydrogen dioxide on an ammoniacal soln. of ammonium dichromate; A. Wesch obtained the same product by treating ammonium chromate in a similar way; and A. Werner added hydrogen dioxide to a cold mixture of a soln. of chromic acid and pyridine; digested the precipitate in 25 per cent. aq. ammonia whereby the triammine was formed. E. H. Riesenfeld found that if red ammonium perchromate is treated with 10 per cent. aq. ammonia at 40°, the soln. furnishes acicular crystals and rhombic plates. These crystals are simply different habits of the same chemical individual, and do not represent two isomeric forms assumed to exist by K. A. Hofmann and H. Hiendlmaier. E. H. Riesenfeld recommended the following mode of preparation:

Add drop by drop 5 c.c. of 30 per cent. hydrogen dioxide to a mixture of 25 c.c. of 10 per cent. aq. ammonia and 5 c.c. of 50 per cent. chromic acid at 0°. When the liquid has been cooled by a freezing mixture for an hour, it is heated to 50° until the rapid evolution of gas has ceased, and the salt has nearly all dissolved. The filtered soln. is cooled to 0°, when brown needles of chromium triamminotetroxide separate out.

O. Wiede, K. A. Hofmann and H. Hiendlmaier, E. H. Riesenfeld and co-workers, A. Werner, and A. Wesch prepared **chromium triamminotetroxide,** $CrO_4.3NH_3$, as previously indicated. The salt appears in brown, doubly refracting prisms; when rapidly cooled, the hot soln. furnishes rectangular plates. O. Wiede reported the axial ratios of the rhombic, pyramidal crystals to be $a:b:c=1\cdot0076:1:1\cdot308$. K. A. Hofmann and H. Hiendlmaier said that there are α- and β-forms respectively with prismatic and tabular crystals; but E. H. Riesenfeld and co-workers showed that both forms have a sp. gr. 1·964 at 15°, and have identical physical properties; and concluded that they are really the same chemical individual. When heated the triamminotetroxide detonates and becomes incandescent forming chromic oxide. Y. Shibata measured the absorption spectrum. Strong acids liberate oxygen and form chromic salts; weak acids—*e.g.* acetic acid—do not change the crystals. E. H. Riesenfeld and co-workers added that the amount of oxygen developed depends on the conc. of the acid. Thus, with dil. acids, most of the oxygen is set free as a gas, and with conc. acids, fully half the oxygen remains in soln. as hydrogen dioxide. If the complex salt be dissolved in aq. ammonia, and then acidified, a transient blue coloration appears, oxygen is evolved, and a green chromic salt soln. is formed. When the complex salt is treated with fixed alkalies, oxygen and ammonia are evolved, and chromate is formed. The triamminotetroxide dissolves in aq. ammonia forming a brown soln., and likewise also in water, but with partial decomposition. The compound is insoluble in all other solvents tried. When 0·1 grm. is covered with alcohol-free ether, and a few drops of dil. sulphuric acid are added, and the mixture shaken, oxygen is evolved and the ether acquires a blue colour. When treated with potassium cyanide, the triamminotetroxide forms $CrO_4.3KCy$; with ethylenediamine, $CrO_4.C_2H_8N_2.2H_2O$; and with hexamethylenetetramine, $CrO_4.C_6H_{12}N_4$.

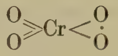
The four types of compounds are closely related chemically; and they can be transformed one into the other. Thus, if an aq. soln. of $(NH_4)_3CrO_8$ is treated with an acid, oxygen is evolved, and $(NH_4)H_2CrO_7$ is formed as a blue soln. and precipitate. If an excess of pyridine be added to either of these salts, $HCrO_5.C_5H_5N$ is formed; and when any of these three salts is treated with an excess of ammonia, the most stable of all the perchromates is produced, namely the triamminotetroxide, $CrO_4.3NH_3$. These changes can be all regarded as a result of the addition or abstraction of hydrogen dioxide. The formation of these compounds by the action of hydrogen dioxide on an aq. or ethereal soln. of chromic acid is taken by E. H. Riesenfeld to mean that the blue soln. does not contain one chemical individual—the $HCrO_5$ of O. Wiede—but rather must it be supposed that *der Grundstoff* is CrO_4 associated with hydrogen dioxide to form $2CrO_4.nH_2O_2$, where n is 1, 3, or 5. Thus, $2CrO_4+H_2O_2=2HCrO_5$; $2CrO_4+3H_2O_2=2H_3CrO_7$; and $2CrO_4+5H_2O_2=2H_2O+2H_3CrO_8$.

Other types have been reported. K. A. Hofmann and H. Hiendlmaier thought that the product obtained by the action of ammonium chromate on hydrogen dioxide in the presence of ammonia had the composition $(NH_4)_2CrO_6$ or $CrO_2(O.ONH_4)_2$, and that when treated with acetic acid it furnished blue $(NH_4)HCrO_6$ or $CrO_2(O.ONH_4)(O.OH)$; but E. H. Riesenfeld and co-workers showed that owing to defective analytical methods the compound with the assigned formula $(NH_4)_2CrO_6$ is identical with red R_3CrO_8; and that $(NH_4)HCrO_6$ is identical with O. Wiede's blue $(NH_4)H_2CrO_7$. H. G. Byers and E. E. Reid said that when the ethereal soln. of the blue perchromate is treated with potassium at −20°, hydrogen is evolved and the purplish-black precipitate produced has the composition **potassium perdichromate**, $KCrO_4$ or $K_2Cr_2O_8$. It is unstable, and rapidly decomposes with evolution of oxygen and the formation of potassium dichromate. By the addition of an alcoholic soln. of potassium cyanide to the blue soln., O. Wiede obtained a similar compound to which he ascribed the formula $KCrO_5.H_2O_2$. When the blue soln. is prepared without employing an excess of hydrogen dioxide, the compound obtained on the addition of potassium cyanide has the same composition as that produced by the action of potassium. The corresponding *sodium, ammonium, lithium, magnesium, calcium, barium, and zinc perdichromates* were prepared. It is inferred, therefore, that the blue ethereal soln. contains **perdichromic acid,** $H_2Cr_2O_8$. When the soln. is prepared in presence of an excess of hydrogen dioxide, it is probable that a more highly oxidized compound is also produced. These conclusions have not been confirmed.

J. A. Raynolds and J. H. Reedy obtained a soln. of red perchromic acid by the action of 30 per cent. hydrogen dioxide on freshly-precipitated chromic hydroxide at 0°; and **calcium perchromate**, $Ca_3(CrO_6)_2.12H_2O$, by adding 30 per cent. hydrogen dioxide to a sat. soln. of calcium chromate at −5° to 0°, or by mixing soln. of calcium acetate and red perchromic acid. The dry salt is a buff powder which explodes at 100°, and when treated with acid, it furnishes blue perchromic acid.

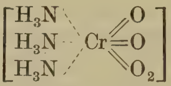
The constitution of the perchromic acids has been investigated by E. H. Riesenfeld and co-workers. Cryoscopic measurements of the R_3CrO_8-salts are in agreement with the simple formula, but, owing to deviations through decomposition, and ionization, the results are equally in agreement with the doubled formula. In benzene soln., the $HCrO_5$-compounds also have a mol. wt. in agreement with the simple formula; and a similar remark applies to the $CrO_4.3NH_3$-compounds in aq. soln. Measurements of the electrochemical eq. of chromium in these soln. were unsatisfactory. It can be assumed that the perchromates contain peroxidic oxygen or the bivalent O_2-group, because, although hydrogen dioxide cannot be detected among the decomposition-products, an alkaline soln. of gold chloride, or potassium permanganate is reduced during the change. These reactions are characteristic of hydrogen dioxide.

It has not been proved whether the chromium in the perchromates is sexivalent or of a higher valency. The chromium in the tetroxide may be sexivalent with a bivalent (–O–O–)-group—*e.g.*:

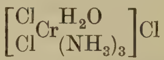


$$\begin{matrix}O\\O\end{matrix}\!\gg Cr < \begin{matrix}O\\ \vdots \\O\end{matrix}$$

The triamminotetroxide can be formulated with the peroxidic oxygen occupying one position in the co-ordinate group:



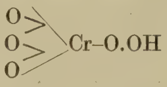
This explains how (i) the compound decomposes into hydrogen dioxide, etc., when treated with acids; (ii) the treatment with an aq. soln. of potassium cyanide furnishes $CrO_4.3KCy$; (iii) the formation of complex chromium ammines observed by E. H. Riesenfeld; and (iv) the treatment with hydrochloric acid in acetic acid soln. furnishes chromic dichloroaquotriamminochloride



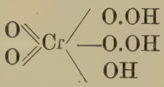
$$\left[\begin{matrix}Cl\\Cl\end{matrix}Cr\begin{matrix}H_2O\\(NH_3)_3\end{matrix}\right]Cl$$

It is not so easy to deal with the other perchromates. Excluding H. G. Byers and E. E. Reid's perdichromates, the perchromate analogue of permonosulphuric acid, H_2SO_5, and perdisulphuric acid, $H_2S_2O_8$, have not been prepared, and consequently the arguments valid with the persulphates cannot, by analogy, be applied to the perchromates. If the formulæ be doubled, the red and blue perchromates can be regarded as derivatives of sexivalent chromium: where $(H_3CrO_8)_2$ becomes $(HO.O)_3:CrO.O.O.CrO(O.OH)_3$, and $(HCrO_5)$ becomes $HO.O.CrO_2.O.O.CrO_2.O.OH$.

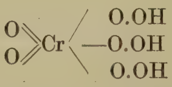
There is no serious objection to this mode of representing the composition of H_3CrO_8 perchromate, but mol. wt. determinations in the case of the $HCrO_5$-perchromate are against the doubled formula. Consequently the chromium probably has a valency higher than six. If nonivalent, $HCrO_5$ becomes $(O{=})_4Cr.O.OH$; H_3CrO_7 becomes $(O{=})_3Cr(OH)_2.O.OH$; and H_3CrO_8 becomes $(O{=})_3Cr(OH){=}(O.OH)_2$; and if septivalent,



Monoperchromic acid, $HCrO_5$.



Diperchromic acid, H_3CrO_7.



Triperchromic acid, H_3CrO_8.

The distinction between septivalent and nonivalent chromium turns on the number of peroxidic or —O.OH radicles. It is not possible to determine the number of peroxidic groups in acidic or alkaline soln. of the perchromate by means of potassium permanganate, because they decompose so rapidly. The red perchromates do not react with permanganate in strongly acid soln., but in alkaline soln. the amount of permanganate reduced increases with the alkalinity of the soln. to a maximum of 5·5 eq. Some peroxidic oxygen probably escapes without acting on the permanganate so that it is assumed that a mol. of the salt gives rise to 3 mols. of hydrogen dioxide. The escape of oxygen without reducing the permanganate is shown by the fact that no appreciable reduction occurs when the red perchromates are decomposed by strongly acidic soln. of permanganate, although oxygen is evolved; and by the fact that the blue perchromates are similarly decomposed in acidic or alkaline soln. of permanganate but only a trace of reduction occurs. This means that there are three peroxidic groups in H_3CrO_8; and this favours the hypothesis that *in the blue perchromates the chromium* is septivalent. This makes the H_3CrO_8-acid, **triperchromic acid,** $(HO.O)_3CrO_2$; the H_3CrO_7-acid, **diperchromic acid,** $(HO.O)_2(HO)CrO_2$; and the $HCrO_5$-acid, **monoperchromic acid,** $(HO.O)CrO_3$. A. R. y Miro found that triperchromic acid, H_3CrO_8, instead of consuming 5 mols of oxygen per mol of dichromate in the reaction $2CrO_8''+12H^{\cdot}=2Cr^{\cdot\cdot\cdot}+6H_2O+5O_2$ actually furnishes 4·6 to 6·5. This is explained by assuming the formation of an acid analogous to $HCrO_5$. Septivalent chromium is not in harmony with the position of chromium in the periodic table ; and it makes chromium an exception to the other elements forming per-acids. If $HO.O.Cr(=O)_3$ be the hydrogen dioxide derivative of a chromic acid, $HO.Cr(=O)_3$, the acid is analogous with permanganic acid, $HO.Mn(=O)_3$. This analogy is supported by the isomorphism between the chromates and manganates ; and between the chromium and manganese alums.

REFERENCES.

[1] Y. Shibata, *Journ. Coll. Science Tokyo*, **41**. 6, 1919 ; L. C. A. Barreswil, *Ann. Chim. Phys.*, (3), **20**. 364, 1848 ; *Compt. Rend.*, **16**. 1085, 1848 ; M. Berthelot, *ib.*, **108**. 24, 157, 477, 1889 ; A. Carnot, *ib.*, **107**. 948, 997, 1888 ; H. Moissan, *ib.*, **97**. 96, 1883 ; E. Péchard, *ib.*, **113**. 39, 1891 ; A. Mailfert, *ib.*, **94**. 860, 1882 ; A. R. y Miro, *Anal. Fis. Quim.*, **18**. 35, 1920 ; W. M. Grosvenor, *Journ. Amer. Chem. Soc.*, **17**. 41, 1895 ; H. Aschoff, *Chem. News*, **5**. 129, 1862 ; *Journ. prakt. Chem.*, (1), **81**. 402, 1860 ; C. F. Schönbein, *ib.*, (1), **80**. 257, 1860 ; G. Werther, *ib.*, (1), **83**. 195, 1861 ; C. Häussermann, *ib.*, (2), **48**. 70, 1893 ; W. P. Jorissen and L. T. Reicher, *Zeit. Farben Textil Chem.*, **2**. 431, 1903 ; F. H. Storer, *Proc. Amer. Acad.*, **4**. 338, 1859 ; *Chem. News*, **1**. 253, 265, 301, 1860 ; C. W. Balke, *Journ. Amer. Chem. Soc.*, **27**. 1156, 1905 ; **30**. 1657, 1908 ; C. Reichard, *Zeit. anal. Chem.*, **40**. 577, 1901 ; **42**. 95, 293, 1903 ; *Chem. Ztg.*, **27**. 12, 27, 1903 ; E. Spitalsky, *Zeit. anorg. Chem.*, **53**. 184, 1907 ; **54**. 184, 1907 ; **57**. 72, 1907 ; **69**. 169, 1910 ; *Ber.*, **43**. 3187, 1910 ; E. H. Riesenfeld, *Zeit. anorg. Chem.*, **74**. 48, 1912 ; *Zur Kenntnis der Ueberchromsäuren*, Freiburg i. Br., 43, 1906 ; *Ber. naturforsh. Ges. Freiburg*, **17**. 1062, 1906 ; *Ber.*, **38**. 3380, 3579, 4068, 1905 ; **41**. 2826, 3536, 3941, 1908 ; **44**. 147, 1911 ; A. Bach, *ib.*, **39**. 872, 1906 ; K. A. Hofmann and H. Hiendlmaier, *ib.*, **37**. 1667, 3405, 1904 ; **38**. 3059, 1905 ; K. A. Hofmann, *ib.*, **39**. 3181, 1906 ; A. Werner, *ib.*, **39**. 2656, 1906 ; **43**. 2286, 1910 ; O. Wiede, *ib.*, **30**. 2178, 1897 ; **31**. 516, 3139, 1904 ; **32**. 3059, 3066, 1905 ; M. Martinon, *Bull. Soc. Chim.*, (2), **45**. 862, 1886 ; E. Baumann, *Zeit. angew. Chem.*, **4**. 135, 1891 ; L. Marchlewsky, *ib.*, **4**. 392, 1891 ; G. Griggi, *L'Orosi*, **18**. 295, 1892 ; H. E. Patten, *Amer. Chem. Journ.*, **29**. 385, 1903 ; H. G. Byers and E. E. Reid, *ib.*, **32**. 503, 1904 ; B. C. Brodie, *Proc. Roy. Soc.*, **11**. 443, 1861 ; T. Fairley, *Journ. Chem. Soc.*, **32**. 1, 125, 1877 ; *Chem. News*, **33**. 238, 1876 ; G. N. Ridley, *ib.*, **127**. 81, 1923 ; E. I. Orloff, *Journ. Russ. Phys. Chem. Soc.*, **44**. 1576, 1598, 1912 ; E. H. Riesenfeld, H. E. Wohlers and W. A. Kutsch, *ib.*, **38**. 1885, 1905 ; H. Ohl, *Ueber die Zersetzung der Chromsäure durch Wasserstoffsuperoxyd und die dabei entstehenden höheren Oxydationsprodukte des Chroms*, Freiburg, 1906 ; H. E. Wöhlers, *Beiträge zur Kenntnis der Ueberchromsäuren*, Freiburg, 1907 ; W. A. Kutsch, *Zur Kenntnis der überchromsauren Salze und ihrer Zersetzung in wässeriger Lösung*, Freiburg, 1907 ; E. H. Riesenfeld, W. A. Kutsch, H. Ohl and H. E. Wolters, *Ber.*, **38**. 3380, 1905 ; *Ber. naturforsch. Ges. Freiburg*, **17**. 43, 1906 ; E. H. Riesenfeld and H. E. Wolters, *ib.*, **17**. 1, 1907 ; E. H. Riesenfeld and A. Wesch, *Ber.*, **41**. 2826, 3536, 1908 ; A. Wesch, *Ueber Chromsäurederivate*, Freiburg i. B., 1908 ; G. Böhm, *Zeit. Kryst.*, **63**. 157, 1926 ; J. A. Raynolds and J. H. Reedy, *Journ. Amer. Chem. Soc.*, **52**. 1851, 1930.

§ 20. Chromium Fluorides

C. Poulenc[1] prepared **chromium difluoride,** or **chromous fluoride,** CrF_2, by the action of hydrogen fluoride on red-hot chromium ; and by the action of hydrogen fluoride on chromous chloride at ordinary temp. A. Mourlot obtained it by the action of hydrogen fluoride on chromous sulphide. G. Herrmann did not obtain good yields in the electrolytic reduction of chromic fluoride soln. K. Jellinek and A. Rudat found that the difluoride is produced by heating the trifluoride in hydrogen : $2CrF_3+H_2\rightleftharpoons 2CrF_2+2HF$. According to C. Poulenc, chromous fluoride forms a grey mass which consists of monoclinic crystals of sp. gr. 4·11. The salt is reduced by hydrogen at a red-heat. K. Jellinek and A. Rudat found that in the reaction $CrF_2+H_2\rightleftharpoons Cr+2HF$, at the absolute temp. 873°, 973°, and 1073°, the values of log (p^2_{HF}/p_{H_2}) are respectively $-3·70$, $-3·02$, and $-2·56$; those of log $(p_{HF}/p_{H_2}p_{F_2})$, 33·12, 29·83, and 27·15 ; and log p_{F_2}, $-36·82$, $-32·85$, and $-29·50$, where p_{F_2} is the vap. press. of the difluoride. The heat of formation is 152 Cals. C. Poulenc observed that the difluoride is transformed into chromic oxide when heated in air. It is sparingly soluble in water. Boiling hydrochloric acid dissolves the salt; and at a red-heat, hydrogen sulphide forms chromous sulphide. The salt is but slightly attacked by hot sulphuric acid, or dil. nitric acid; it is insoluble in alcohol; and forms chromic oxide and finally chromate when fused with alkali carbonates.

W. Traube and co-workers prepared **ammonium chromous fluoride,** $NH_4CrF_3.2H_2O$, from soln. of chromous acetate and ammonium hydrofluoride dissolved in very little water. The soln. gradually deposits a pale blue powder which is fairly stable in dry air, and forms a pale blue soln. with water. Dil. nitric acid oxidizes it with the evolution of nitrogen oxides. They also prepared **potassium chromous fluoride,** $KCrF_3$, in an analogous manner.

If dry chromic oxide, not previously calcined, be treated with an excess of hydrofluoric acid, and the soln. evaporated to dryness and strongly heated, **chromium trifluoride,** or **chromic fluoride,** CrF_3, is formed. H. St. C. Deville obtained it by passing hydrogen fluoride over a mixture of fluorspar and chromic oxide heated to redness in a carbon tube; and C. Poulenc said that by heating anhydrous chromic chloride, hydrated chromic fluoride or amorphous chromic fluoride, to 1200° in a current of hydrogen fluoride, when crystals of anhydrous chromic fluoride are formed. The dark green, needle-like crystals were found by C. Poulenc to have a sp. gr. of 3·78, and to melt over 1000°. H. St. C. Deville said that the salt melts at a high temp., and volatilizes only a little at the m.p. of steel; it sublimes at the highest temp. of the gas-blowpipe, forming regular octahedra. C. Poulenc found that the salt sublimes at 1100°–1200°. A. Speransky found that the lowering of the f.p. in conc. aq. soln. corresponds with the existence of both simple molecules, CrF_3, and doubled molecules, Cr_2F_6. E. Petersen gave for the heat of formation in aq. soln., $Cr_2O_3+6HF_{aq.}=2CrF_{3aq.}+3H_2O+50{\cdot}3$ Cals. H. von Wartenberg gave $(Cr,\frac{3}{2}F_{2aq.})=171{\cdot}3$ Cals. for the anhydrous trifluoride. G. Magnanini studied the absorption spectrum; and A. Speransky found that the electrical conductivity of aq. soln. shows that only a small proportion of the salt is ionized. The soln. of the violet modification conducts electricity three times better than that of the green. G. Gore electrolyzed a conc. soln. of chromic fluoride acidified with hydrofluoric and hydrochloric acids, and found that the liquid became hot; no gas was liberated at the cathode, but chlorine and ozone were liberated at the platinum anode which was not corroded. C. Poulenc showed that the salt is reduced by hydrogen at dull redness. The heat of formation is 230·95 Cals. per mol—*vide infra,* the dichloride. Steam transforms chromic fluoride into chromic oxide. Chromic fluoride is insoluble in water, and alcohol; hydrogen chloride transforms it into chromic chloride; hot hydrochloric, sulphuric, and nitric acids attack chromic fluoride only a little; hydrogen sulphide converts it into black sulphide; and molten alkali nitrate or carbonate converts it into chromate. A. Costachescu prepared complex pyridine salts.

According to J. J. Berzelius, brown chromic chromate forms a rose-coloured soln. when treated with hydrofluoric acid; and the soln. dries to a rose-coloured salt which dissolves in water and gives a brown precipitate with ammonia. E. Petersen observed that if chromium, or hydrated chromic oxide be dissolved in hydrofluoric acid, and the soln. evaporated, there remains a green, crystalline mass, soluble in water. G. Herrmann studied the electrolytic reduction of soln. of chromic fluoride. A. Werner and W. Costachescu obtained the insoluble green *trihydrate,* $CrF_3.3H_2O$, or $[Cr(H_2O)_6]CrF_6$, by heating the hexahydrate with water on a water-bath. That part which becomes insoluble is the trihydrate. It is also formed by heating the hemiheptahydrate to 105°. C. Poulenc obtained the *hemiheptahydrate,* $CrF_3.3\frac{1}{2}H_2O$, by pouring an aq. soln. of the fluoride into hot alcohol. The salt is a green crystalline powder which can be obtained in small prisms by allowing the soln. to diffuse slowly into one another. It is soluble in water. A. Werner and W. Costachescu obtained another form of the hemiheptahydrate by double decomposition between the hexahydrated chloride and ammonium chromium hexafluoride. The pale green, crystalline powder loses a mol. of water at 105°. This salt is represented by the formula $[Cr(H_2O)_6]CrF_3].H_2O$, and it is considered to be isomeric with the tetrahydrate, which is regarded as the monohydrated **chromic triaquotrifluoride,** $[F_3\equiv Cr\equiv(H_2O)_3]H_2O$, whose aq. soln. has an acid reaction, and does not give the reactions of fluorides. The electrical conductivities of a mol of the salt in 100, 500, and 1000 litres of water are, respectively, 22, 26·6, and 31·0. A. Loesche's analysis corresponds with $Cr_3F_8.11H_2O_4$, or $CrF_2.Cr_2F_6.11H_2O$. A. Hiendlmayr prepared **chromic aquopentamminotrifluoride,** $[Cr(NH_3)_5(H_2O)]F_3$, by the action of hydrofluoric acid on the corresponding hydroxide. If the yellow compound be allowed to stand in contact with its mother-liquor, it furnishes **chromic fluopentamminodifluoride,** $[Cr(NH_3)_5F]F_2$, as a flesh-coloured precipitate which dries to a carmine-red powder. R. Köpp obtained what he regarded as a *tetrahydrate*, from a soln. of hydrated chromic oxide in hydrofluoric acid, and he recommended it for use as a mordant. It was probably imperfectly dried hemiheptahydrate. A. Werner and W. Costachescu treated a soln. of 20 grms. of violet chromic nitrate in the smallest possible quantity of water, with a conc. soln. of 8·69 grms. of potassium fluoride, and washed the crystalline mass of violet *hexahydrate*, $CrF_3.6H_2O$, or **chromic hexaquofluoride,** $[Cr(H_2O)_6]F_3$. The salt was dried first by press. between bibulous paper, and afterwards in a desiccator for 3–4 days over conc. sulphuric acid. The salt loses 3 mols. of water at 60°–70° in 8 hrs., and more at a higher temp., and it then decomposes. The salt is sparingly soluble in water, and is hydrolyzed in aq. soln. The electrical conductivity, μ mhos, of a mol of the salt in v litres at 18°, is μ=152·1 for v=100; μ=196·5 for v=500; and μ=223 for v=1000—about half that of the violet chloride. The conductivity does not change with time. When treated with sulphuric acid, it forms chromic hexaquosulphate. When the moist crystals are kept, they pass into the *enneahydrate*, $CrF_3.9H_2O$, or $[Cr(H_2O)_6]F_3.3H_2O$. The conversion occurs spontaneously when the crystals are washed, or pressed slightly with a spatula. G. Fabris prepared the enneahydrate, by treating a soln. of violet chromic sulphate with ammonium fluoride—not in excess. When the salt is heated, water is evolved, and the residue is green. The violet crystals are sparingly soluble in water; and insoluble in alcohol, and in a soln. of ammonium fluoride; the soln. in hydrochloric acid is violet; that in potash-lye is green. F. Hein and co-workers, and R. Weinland and W. Hübner, studied some complexes with organic compounds. F. Pintus prepared the complex with pyridine, chromic tripyridinofluoride, $[CrPy_3F_3]$; and E. Wilke-Dörfurt and H. G. Mureck, **chromic hexantipyrinoborofluoride,** $[Cr(COC_{10}H_{12}N_2)_6](BF_4)_3$.

J. J. Berzelius prepared ammonium, potassium, and sodium chromium fluorides as green sparingly soluble powders, but he did not give an analysis. R. Wagner found that **ammonium chromium pentafluoride,** $(NH_4)_2CrF_5.H_2O$, is formed when ammonia is passed into an aq. soln. of chromic fluoride, and the product extracted with absolute alcohol. Emerald-green, octahedral crystals are formed by treating the product with hydrofluoric acid. A. Werner and A. Gubser represent this salt as *ammonium aquopentafluoride*, $[Cr(H_2O)F_5](NH_4)_2$. R. Wagner, A. Werner and W. Costachescu, and E. Petersen obtained **ammonium chromium hexafluoride,** $3NH_4Cl.CrF_3$, by mixing soln. of chromic and ammonium fluorides; H. von Helmolt, by the action of a hot soln. of ammonium fluoride on freshly precipitated chromic oxide; and G. Fabris, by warming violet chromic sulphate with an excess of ammonium fluoride. The green, octahedral crystals are freely soluble in water, and sparingly soluble in a soln. of ammonium fluoride. A. Werner and A. Gubser represent this salt by the formula $[CrF_6](NH_4)_3$. R. F. Weinland and co-workers prepared the guanidine salt, $[CrF_6]H_3.3CH_5N_3$. R. Wagner prepared **sodium chromium pentafluoride,** $2NaF.CrF_3.\frac{1}{2}H_2O$, as a green, sparingly soluble powder, from a mixed soln. of sodium and chromic fluorides. A. Moberg observed that a soln. of chromic fluoride gives a green precipitate when treated with potassium fluoride. O. T. Christensen, and R. Wagner prepared **potassium chromium**

pentafluoride, $2KF.CrF_3.H_2O$, in green crystals, insoluble in water, and soluble in conc. hydrochloric acid. O. T. Christensen, and C. Poulenc also prepared **potassium chromium hexafluoride,** K_3CrF_6, from a mixed soln. of chromic fluoride and potassium hydrofluoride, or by melting a mixture of these two salts, and extracting the mass with hydrofluoric acid. A. Duboin obtained crystals of the salt by adding chromic oxide or fluoride to molten potassium hydrofluoride. The green crystals of the complex salt have a sp. gr. 2·93 at 0°. The green crystals are insoluble in water, and are not decomposed by a boiling soln. of sodium carbonate. A. Duboin said that the crystals are freely soluble in nitric and hydrochloric acids. G. O. Higley prepared **copper chromium pentafluoride,** $CuCrF_5.5H_2O$, by evaporating a soln. of eq. molar proportions of copper and chromium fluorides in hydrofluoric acid; and recrystallization from hydrofluoric acid. The salt loses water at 200°. He also obtained **zinc chromium pentafluoride,** $ZnCrF_5.7H_2O$, in an analogous manner. F. Ephraim and P. Barteczko prepared **thallous chromium enneafluoride,** $3TlF.2CrF_3$, by evaporating a mixed soln. of chromic and thallous fluorides. It forms a green, crystalline powder.

References.

[1] C. Poulenc, *Compt. Rend.*, **116**. 253, 1893; *Ann. Chim. Phys.*, (7), **2**. 60, 1894; A. Mourlot, *ib.*, (7), **17**. 544, 1899; W. Traube, E. Burmeister and R. Stahn, *Zeit. anorg. Chem.*, **147**. 50, 1925; K. Jellinek and A. Rudat, *ib.*, **175**. 281, 1928; A. Rudat, *Ueber die Fluortensionen von Metallfluoriden und die chemischen Konstanten von Fluor und Fluorwasserstoff*, Danzig, 1928; G. Herrmann, *Ueber die elektrolytische Darstellung von Chromosalzen*, München, 57, 1909.

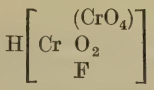
[2] H. St. C. Deville, *Compt. Rend.*, **43**. 970, 1856; *Ann. Chim. Phys.*, (3), **49**. 85, 1857; C. Poulenc, *ib.*, (7), **2**. 62, 1894; *Compt. Rend.*, **116**. 254, 1893; A. Duboin, *ib.*, **181**. 336, 1925; F. Hein, J. Reschke and F. Pintus, *Ber.*, **60**. B, 679, 1927; A. Moberg, *Dissertatio de chloretochromoso*, Helsingfors, 1843; *Journ. prakt. Chem.*, (1), **29**. 175, 1843; A. Speransky, *Journ. Russ. Phys. Chem. Soc.*, **24**. 304, 1892; G. Magnanini, *Gazz. Chim. Ital.*, **25**. ii, 378, 1895; G. Fabris, *ib.*, **20**. 582, 1890; *Atti Accad. Lincei*, (4), **6**. i, 576, 1890; A. Hiendlmayr, *Beiträge zur Chemie der Chrom- und Kobalt-Ammoniake*, Friesing, 17, 1907; O. T. Christensen, *Journ. prakt. Chem.*, (2), **35**. 163, 1887; (2), **40**. 60, 1889; *Zeit. phys. Chem.*, **4**. 408, 1889; G. O. Higley, *Journ. Amer. Chem. Soc.*, **26**. 629, 1904; G. Herrmann, *Ueber die elektrolytische Darstellung von Chromosalzen*, München, 57, 1909; J. J. Berzelius, *Pogg. Ann.*, **1**. 34, 1824; F. Ephraim and P. Barteczko, *Zeit. anorg. Chem.*, **61**. 238, 1909; H. von Wartenberg, *ib.*, **151**. 326, 1926; R. Köpp, *German Pat.*, *D.R.P.* 44493, 1887; R. Wagner, *Ber.*, **19**. 896, 1886; A. Werner and A. Gubser, *ib.*, **34**. 1603, 1901; *Liebig's Ann.*, **322**. 345, 1902; A. Werner, *Zeit. anorg. Chem.*, **3**. 293, 1893; R. F. Weinland, I. Lang, and H. Fikentscher, *ib.*, **150**. 47, 1925; A. Werner and W. Costachescu, *Ber.*, **41**. 4242, 1908; W. Costachescu, *Ann. Univ. Jassy*, **7**. 87, 1912; **8**. 16, 1914; H. von Helmolt, *Zeit. anorg. Chem.*, **3**. 125, 1893; R. Weinland and W. Hübner, *ib.*, **178**. 275, 1929; K. Jellinek and A. Rudat, *ib.*, **175**. 281, 1928; A. Rudat, *Ueber die Fluortensionen von Metallfluoriden und die chemischen Konstanten von Fluor und Fluorwasserstoff*, Danzig, 1928; A. Loesche, *Ueber Verbindungen von Eisen und Chrom mit Fluorwasserstoffsäure*, Weida i. Th., 1909; F. Pintus, *Ueber die Existenz des einwertigen Chroms und den Einfluss der Komplexkonstitution auf die Bildung chromorganischer Verbindungen*, Leipzig, 1928; E. Petersen, *Journ. prakt. Chem.*, (2), **40**. 60, 1889; E. Wilke-Dörfurt and H. G. Mureck, *Zeit. anorg. Chem.*, **184**. 121, 1929; G. Gore, *Electrochemistry*, London, 96, 1906.

§ 21. Chromium Oxyfluorides

O. Unverdorben [1] prepared what was thought to be a higher chromium fluoride by distilling in a platinum or lead retort a mixture of equal parts of lead chromate and fluorspar and 3 parts of fuming sulphuric acid. H. Rose employed potassium dichromate instead of lead chromate. It was discovered by V. Oliveri, in 1886, that the product is not chromic fluoride at all, but rather **chromium dioxydifluoride,** CrO_2F_2. The bivalent CrO_2-radicle is sometimes called the chromyl-radicle, so that the compound is also named **chromyl fluoride.** W. P. Evans used O. Unverdorben's process; and C. L. Jackson and G. T. Hartshorn, and V. Oliveri, H. Rose's process. O. Ruff heated antimony pentafluoride and chromyl chloride and obtained a yellow gas thought to be chromyl fluoride. The red vapour of chromyl fluoride, said O. Unverdorben, produces severe oppression of the lungs; and J. B. A. Dumas found that when cooled, the vapour condenses to a red liquid. O. Unverdorben observed that the vapour is decomposed by water with the evolution of heat forming chromic and hydrofluoric acids; and when exposed to air, it forms a yellow cloud, and deposits crystals of chromium trioxide. Chromyl fluoride combines with ammonia; it converts arsenic trioxide into arsenic trifluoride and chromium trioxide; boric oxide forms boron trifluoride and chromium trioxide; and silica and even glass form silicon tetrafluoride and chromium trioxide. Organic substances are destroyed by the vapour; alcohol and ether form chromium trifluoride; and F. Wöhler said that when the vapour is passed into absolute alcohol a brownish-green powder is deposited and heat is evolved. C. L. Jackson and G. T. Hartshorn found that benzoic acid is converted into difluobenzoic acid; and V. Oliveri, that toluene reacts as in the case of chromyl chloride, forming a black mass, which, with water, gives benzaldehyde. O. Unverdorben found that mercury slowly decomposes the vapour of chromyl fluoride; and W. P. Evans found that zinc or sodium reduces the vapour to chromium (*q.v.*).

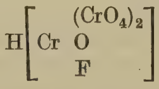
L. Varenne treated a nitric acid soln. of ammonium trichromate with hydrofluoric acid, and obtained red, efflorescent crystals of **ammonium dichromyl tetrafluochromate,** $(NH_4)_2CrO_4.2CrO_2F_2$. The crystals attack glass; and they are decomposed by acids, forming hydrofluoric and chromic acids. If ammonium dichromate be used instead of the trichromate, L. Varenne obtained **ammonium chromyl difluochromate,** $(NH_4)_2CrO_4.CrO_2F_2$, which can be regarded as **ammonium fluochromate,** NH_4CrO_3F, the salt of a hypothetical *fluochromic acid*, $HCrO_3.F$. The red crystals change slowly when exposed to air; they attack glass; and are decomposed by heat. A. Werner [2] represented the salt by $NH_4[CrO_3F]$. A. Streng boiled potassium dichromate with conc. hydrofluoric acid, and on cooling the clear soln., obtained ruby-red crystals of **potassium fluochromate,** $KCrO_3F$. L. Varenne obtained the salt by a similar process; and A. Ditte, by cooling a hot soln. of potassium fluoride and chromic acid in eq. proportions. A. Streng, and L. Varenne said that the crystals become reddish-yellow and melt when exposed to air; they cannot be preserved in glass vessels; they melt when heated, forming a dark brown liquid, and at a red-heat lose 11 per cent. in weight; at a still higher temp. in glass vessels, oxygen is evolved and silicon tetrafluoride is formed. A. C. Oudemans said that the salt decomposes as in the analogous case of the chlorochromates. A. Streng, and L. Varenne found that the salt is soluble in water, and boiling water converts the salt into potassium dichromate and hydrofluoric acid. The salt can be recrystallized from a little water; with sulphuric acid it forms hydrofluoric and chromic acids; and with alkalies, potassium fluoride and chromate are formed. F. Olsson prepared **potassium dioxydifluochromate,** $KF.CrO_2F.H_2O$, as a yellowish-brown precipitate by adding an aq. soln. of $4CrO_3.Cr_2O_3$ to an excess of a soln. of potassium fluoride in 40 per cent. hydrofluoric acid at 0°. This is thought to be a complex containing quinquevalent chromium.

R. Weinland and H. Staelin prepared a series of fluochromates which are represented on the co-ordination theory by the formulæ $H[CrO_3F]$ in the simplest case, analogous to $H_2[CrO_4]$ for the chromates. The fluochromates are represented by pyridine, quinoline, guanidine and **tetramethylammonium fluochromate,** $[CrO_3F]N(CH_3)_4$; and by **silver fluochromate,** $Ag[CrO_3F]$, obtained as a dark red, sparingly soluble powder by mixing a soln. of chromic acid with hydrofluoric acid, and silver acetate. They prepared **thallous fluochromate,** $Tl[CrO_3F]$, in an analogous way as a brownish-yellow powder sparingly soluble in water. Comparing the formula, $H[CrO_3F]$, with those for the polychromic acids—*vide supra*—there follow:



$$H\left[Cr\begin{matrix}(CrO_4)\\O_2\\F\end{matrix}\right]$$

Fluodichromates.



$$H\left[Cr\begin{matrix}(CrO_4)_2\\O\\F\end{matrix}\right]$$

Fluotrichromates.

The **fluodichromates** are represented by ethylenediamine fluodichromate,

$H[Cr(CrO_4)(O_2)F].en$; and the **fluotrichromates** by pyridine and quinoline fluotrichromates. A. Hiendlmayr[3] prepared **chromic fluopentamminochromate,** $[Cr(NH_3)_5F]CrO_4$, from a conc. soln. of the fluoride and potassium chromate. R. Weinland and co-workers prepared complex salts of the fluoride with pyridine, *o*-toluidine, guanidine, and aniline.

REFERENCES.

[1] O. Unverdorben, *Trommsdorff's Journ.*, **9**. 26, 1824; *Pogg. Ann.*, **7**. 311, 1826; H. Rose, *ib.*, **27**. 565, 1833; J. J. Berzelius, *ib.*, **1**. 34, 1824; F. Wöhler, *ib.*, **33**. 343, 1834; W. P. Evans, *Zeit. angew. Chem.*, **4**. 18, 1891; F. Olsson, *Arkiv Kem. Min. Geol.*, **9**. 10, 1924; V. Oliveri, *Gazz. Chim. Ital.*, **16**. 218, 1886; J. B. A. Dumas, *Ann. Chim. Phys.*, (2), **31**. 435, 1826; C. L. Jackson and G. T. Hartshorn, *Amer. Chem. Journ.*, **7**. 343, 1885; *Ber.*, **8**. 1993, 1885; O. Ruff, *ib.*, **39**. 4316, 1906; **47**. 656, 1914; L. Varenne, *Compt. Rend.*, **91**. 989, 1880; **93**. 728, 1881.

[2] A. Streng, *Liebig's Ann.*, **129**. 225, 1864; L. Varenne, *Compt. Rend.*, **89**. 358, 1879; A. Ditte, *ib.*, **134**. 337, 1902; A. C. Oudemans, *Rec. Trav. Chim. Pays-Bas*, **5**. 116, 1886; A. Werner, *Zeit. anorg. Chem.*, **9**. 407, 1895; R. Weinland and H. Staelin, *ib.*, **136**. 313, 1924; F. Olsson, *Arkiv Kem. Min. Geol.*, **9**. 10, 1924.

[3] A. Hiendlmayr, *Beiträge zur Chemie der Chrom- und Kobalt-Ammoniake*, Friesing, 17, 1907; R. Weinland and J. Lindner, *Zeit. anorg. Chem.*, **190**. 285, 1930; R. Weinland and W. Hübner, *ib.*, **178**. 275, 1929.

§ 22. Chromium Chlorides

F. Hein and co-workers,[1] and F. Pintus obtained evidence of the formation of a transient **chromium monochloride,** CrCl, in their study of the action of magnesium phenyl bromide on chromic chloride: $4Mg(C_6H_5)Br+3CrCl_3=Cr(C_6H_5)_4Cl+2MgBr_2+2MgCl_2+2CrCl_2$; followed by $4CrCl_2+4Mg(C_6H_5)Br=Cr(C_6H_5)_4Cl+3CrCl+2MgCl_2+2MgBr_2$—the initial evolution of hydrogen as attributed to the action of the monochloride.

A. Moberg prepared **chromium dichloride,** or **chromous chloride,** $CrCl_2$, by passing dry hydrogen over heated violet chromic chloride as long as hydrogen chloride is given off. If the temp. be too high, A. Moberg, W. Gregory, and J. J. Berzelius found that chromium is produced. The hydrogen must be freed from traces of oxygen: to do this, A. Moberg passed the hydrogen over heated spongy platinum, while E. M. Péligot scrubbed the gas with a soln. of stannous chloride in potash-lye. E. M. Péligot observed that it may be formed at the same time as the trichloride when dry chlorine is passed over a red-hot mixture of chromic oxide and charcoal. C. E. Ufer, H. Moissan, and I. Koppel obtained chromous chloride by passing hydrogen chloride over chromium at a high temp. T. Döring showed that the reaction, $2CrCl_3+H_2=2HCl+2CrCl_2$, is irreversible. H. Moissan also obtained chromous chloride by heating chromic chloride in the vapour of ammonium chloride; and A. Recoura, by dehydrating the hydrates at 250° in a current of nitrogen—W. A. Knight and E. M. Rich worked at 180° in vacuo. F. Wöhler observed that an aq. soln. of chromous chloride is formed by dissolving chromium in hydrochloric acid; H. Löwel, H. Moissan, and A. Recoura, by reducing a soln. of chromic chloride with zinc; and K. Someya, by reducing soln. of chromic salts with zinc- or lead-amalgam. G. Herrmann studied the electro-reduction of soln. of chromic chloride to chromous chloride and obtained the following yields at 50°–60°:

Current density	. .	1	2	3	4	5 amps.
Efficiency	Pt electrode .	16	35	67	50	25 per cent.
	Pb electrode .	95	81	65	45	25 ,,

W. Traube and co-workers prepared conc. soln. of chromous chloride by the prolonged electrolytic reduction of aq. soln. of green chromic chloride, using lead plates as electrodes and employing a current desnity of 0·175 amp. per sq. dm. The electrolysis of chromous chloride soln., using an iron cathode, results in the formation of a cathodic deposit of metallic chromium mixed with chromium oxides.

W. Traube and A. Goodson protected the soln. from air during electrolysis by covering them with light petroleum ; they found that the most favourable conditions for the economic reduction are the electrolysis of the violet chromic salts in moderately acid conc. soln., using a lead cathode, and a current density of about 2·5 amp. per sq. dm. The more common green salts, in aq. soln., require a greater expenditure of current than the violet salts, but they yield much more conc. soln. and are, therefore, more suitable in the end for the production, at any rate, of soln. rich in chromous salts but not entirely free from chromic salts. The same slower reduction of the green complexes is observed when soln. are treated with zinc. M. C. Taylor and co-workers found that in a two-compartment cell with a spiral, spongy lead cathode, and five graphite anodes, a soln. of chromic chloride is reduced to chromous chloride. With a total cathode surface of 1·24 sq. dm. and a current of 1·6 amps. a current efficiency of 96 per cent. may be obtained over the period required to reduce 87 per cent. of the chromium if the soln. is rapidly stirred and if the current is reduced when hydrogen commences to be evolved. With an unchanged current the efficiency is only 53 per cent. for the same amount of reduction. F. Hein and co-workers found that phenyl magnesium bromide reacts with chromic chloride, forming chromous chloride, $3CrCl_3+4C_6H_5MgBr=(C_6H_5)_4CrCl+2MgBr_2+2MgCl_2+2CrCl_2$; and that the reduction proceeds further, forming **chromium monochloride,** CrCl, thus, $4CrCl_2+4C_6H_5MgBr=(C_6H_5)_4CrCl+3CrCl+2MgCl_2+2MgBr_2$. H. Moissan said that if the aq. soln. be evaporated, it deposits crystals of the *hexahydrate ;* but A. Recoura, and W. A. Knight and E. M. Rich observed that it is the *tetrahydrate* that is formed under these conditions—*vide infra.*

Analyses of the anhydrous salt were made by A. Moberg, H. Moissan, E. M. Péligot, and A. Recoura. K. Someya discussed the colour of chromous salt soln. Chromous chloride may furnish white pseudomorphs after chromic chloride ; it may form white needles ; or colourless radiating masses. F. W. Clarke and J. P. Grabfield gave 2·751 for the sp. gr. at 14°/4° ; and W. Biltz and E. Birk, 2·878 at 25°/4°. For the mol. vol., *vide infra,* hydrated chromic chloride. A. Moberg said that the salt is readily melted. L. F. Nilson and O. Pettersson found the vap. density (air unity) to be 7·80 between 1300° and 1400° ; 7·27 between 1400° and 1500° ; and 6·22 between 1500° and 1600°. The theoretical value for $CrCl_2$ is 4·256. The decrease which occurs with a rise of temp. indicates that the dissociation of more complex molecules is approaching completion. A. Recoura gave for the heat of hydration : $CrCl_{2solid} \rightarrow CrCl_2.4H_2O_{cryst.}+16{\cdot}6$ Cals. ; and for the heat of soln., 18·6 Cals. K. Jellinek and R. Koop found for the reaction $Cr+Cl_2=CrCl_2$, 76·68 Cals. F. Allison and E. J. Murphy studied the magneto-optic properties. W. Hampe found that molten chromous chloride is an electrical conductor, and on electrolysis, chromium separates at the negative pole. H. Küssner found that a chromium anode in soln. of potassium chloride dissolves with different valencies between 2 and 6. At low temp. and small current densities, the valency approaches 6, but at higher temp. no conditions could be found which gave only one kind of ion. Similar results were obtained with alcoholic soln. of zinc chloride. S. Meyer gave 47×10^{-6} mass units for the magnetic susceptibility ; and R. H. Weber gave for the atomic magnetism 0·0182. B. Cabrera and S. P. de Rubies studied this subject. G. Breit and H. K. Onnes found that the order of the magnetic susceptibility is unchanged when the frequency of alternation of the magnetic field is increased to 369,000, for the value in the alternating field is 0·75 of the value for the direct field.

The reaction $CrCl_2+H_2=2HCl+Cr$ was studied by K. Jellinek and R. Koop. The anhydrous salt is stable in dry air, but it deliquesces in moist air and becomes green owing to oxidation. The autoxidation of soln. of chromous chloride in the absence of air with the development of hydrogen was studied by A. Moberg, H. Moissan, and A. Recoura. M. Berthelot observed that the change is accelerated by acids ; and T. Döring, that it is accelerated by precipitated gold ; and W. Traube and co-workers, that it is accelerated by palladium salts. A. Asmanoff showed that the reaction is accelerated by platinum in the presence of hydrochloric acid; and with sulphuric acid the reaction is slower. The unimolecular reaction with 0·1N-HCl at 29·4° has a velocity constant of 0·0129; and with 0·1N-H_2SO_4, 0·0115. Without platinum the evolution of hydrogen with 10N- sulphuric acid cannot be detected, but it can be observed with hydrochloric acid. Ammonium chloride in N-HCl gives a measurable yield of hydrogen even when platinum is absent. The reaction proceeds more rapidly in ammoniacal soln., and is fastest in soln. containing ammonium sulphate. The speed of the reaction increases as the conc. of the ammonia increases. The reaction in ammoniacal soln. is accelerated by chromic salts. W. Traube and W. Lange found that the conversion of chromous to chromic salts is accelerated by a metal of the platinum group, or by a hydrogen acceptor, as well as by substances which cannot be regarded as hydrogen acceptors. The reaction is interpreted according to the scheme $Cr(OH)_2 \rightarrow Cr(:O).OH+H$. The reaction was studied by H. Wieland and F. G. Fischer. E. S. Hedges and J. E. Myers showed that the evolution of hydrogen in the autoxidation of chromous chloride in the presence of platinum may be periodic, chromous chloride dissolved in *water* with the evolution of much heat forming a blue soln. which rapidly turns green owing to the absorption of oxygen, and, according to E. M. Péligot, the formation of Cr_2OCl_2—a reaction which A. Recoura found to be attended by the evolution of 100·8 Cals. Soln. of chromous chloride were used by F. O. von der Pfordten, R. P. Anderson and J. Riffe, W. Manchot and J. Herzog, for the absorption of *oxygen* in gas analysis—*vide* **8**. 49, 1. A. Mailfert studied the action of ozone. Chromous chloride is transformed into chromic chloride by *chlorine*, and A. Recoura gave for the heat of the reaction $(CrCl_{2solid}, Cl_{gas})$=39·4 Cals.; $(CrCl_{2soln.}, Cl_{gas}) = CrCl_{3green\ soln.}+51{\cdot}4$ Cals.; and $(CrCl_{soln.}, Cl_{gas})=CrCl_{3violet\ soln.}+60{\cdot}8$ Cals. G. S. Forbes and H. W. Richter dissolved chromous chloride in ice-cold 0·1N-HCl in an atm. of hydrogen or carbon dioxide free from all traces of oxygen. The mercury or platinum potential rose continuously to a maximum value which became constant after two days. If traces of oxygen are present, the potential fluctuated irregularly. When referred to the hydrogen electrode as zero, at 25°, $E=-0{\cdot}400+0{\cdot}065 \log (Cr'''/Cr'')$. The maximum potential with platinum was about 0·16 volt lower than with mercury, and hydrogen was evolved. G. Herrmann studied the electrolytic reduction of soln. of chromic chloride. If *hydrogen chloride* is passed for a long time into a conc. soln. of chromic chloride, cooled to 0°, a bluish powder of *chromous hydrochloride*, $3CrCl_2.2HCl.13H_2O$, is formed; it is stable at 0°, but decomposes at 20°. A. Moberg, and E. M. Péligot found that the blue aq. soln. gives a pale green precipitate with *potassium fluoride*, but no precipitate with *potassium bromide, or iodide*. V. Rothmund, and R. Stahn studied the reduction of *perchlorates* by chromous salts. E. M. Péligot obtained a black precipitate with *potassium sulphide*—it is insoluble in an excess of the alkali sulphide. *Potassium sulphite* gives a brick-red precipitate. A. Moberg said that *ammonia* gives a pale blue precipitate and a little hydrogen is evolved—the supernatant blue soln. becomes red in air—but E. M. Péligot said that no hydrogen is given off; and added that a mixture of ammonia and ammonium chloride gives a blue soln. which becomes red on exposure to air. W. Peters found that chromous chloride absorbs ammonia, forming ash-grey **chromous hexamminodichloride,** $CrCl_2.6NH_3$, and when this is kept in vacuo it forms a violet **chromous triamminodichloride,** $CrCl_2.3NH_3$. W. Biltz and E. Birk found that the sp. gr. of the hexamminodichloride is 1·392 at 25°/4°. F. Ephraim and S. Millmann discussed the stability of these salts; and W. Biltz and E. Birk, the mol. vols. K. Kraut described the formation of some chromous ammines—*vide infra*. W. Traube and W. Passarge prepared lilac-coloured **chromous dihydrazinochloride,** $CrCl_2.2N_2H_4$, by precipitation on adding a soln. of hydrazine hydrate to a soln. of the chloride. The precipitate is washed with water, alcohol, and ether, and dried over sulphuric acid. R. Stahn studied the reduction of *potassium azide* by chromous salts. W. Traube and W. Passarge found that chromous salts reduce *nitrous* oxide in the presence of alkali hydroxide to nitrogen; *nitric acid*, and *hydroxylamine* are reduced quantitatively to ammonia, but the reduction of *nitrous acid* to ammonia is not quantitative. For the action of *nitric oxide*, studied by G. Chesneau, J. Sand and O. Burger, and V. Kohlschütter, *vide* **8**. 49, 35. A. Moberg found that *sodium hydrophosphate* gives a blue precipitate; and sodium carbonate gives a yellowish-green precipitate and the supernatant liquor becomes yellow. W. Traube and W. Passarge showed that soln. of chromous salts are gradually oxidized, especially in acidic soln., with the liberation of hydrogen: $2CrO+H_2O=Cr_2O_3+H_2$; in consequence, they are able in the presence of water to reduce compounds with double or triple linkages. Thus, they reduce *acetylene* to ethylene, but not *ethylene* to ethene; maleic and fumaric acids are reduced to succinic acid in acidic and alkaline soln.; *cinnamic and phenylpropionic acids* yield β-phenyl propionic acid with an alkaline suspension of chromous oxide; and *benzaldoxime* is transformed into benzylamine. E. M. Péligot found that *potassium thiocyanate* gives no precipitate. R. Stahn studied the reduction of *thiocyanic acid*, and of *potassium cyanide*. R. Ripan discussed the hydrolysis of chromic salts by potassium cyanate. J. J. Berzelius found that potassium cyanide gives a white precipitate insoluble in excess; E. M. Péligot found that *potassium ferrocyanide* gives a yellowish-green precipitate; and *sodium acetate*, red crystals of chromous acetate. R. Stahn studied the reduction of *chloroacetic acid* and of *oxalic acid;* and A. Moberg found that *potassium oxalate* gives a grey bluish-green precipitate; *sodium formate* has no visible action; *potassium tartrate* has no action; *sodium citrate* gives a violet-red precipitate which slowly dissolves; *potassium succinate* gives a scarlet-red precipitate; *potassium benzoate*, a pale red precipitate; and *sodium tetraborate*, a pale blue precipitate. R. Stahn studied the reduction of *benzaldehyde*. A. Moberg observed that *potassium hydroxide* gives a yellow precipitate, and, added E. M. Péligot, if kept out of contact with air it gives a brown precipitate of hydrated chromous oxide (*q.v.*) accompanied by the evolution of hydrogen. W. Traube and co-workers found that the precipitation of soln. of chromous salts by alkali-lye gives a mixture of hydrated chromous and chromic oxides in varying proportions. E. M. Péligot regarded chromous chloride as one of the most powerful of reducing agents. For instance, it gives a brown precipitate of chromic chromate when treated with *potassium monochromate; cupric salt* soln. furnish first cuprous chloride, and afterwards with an excess of chromous salt, a red precipitate of cuprous oxide or copper; E. Zinth and G. Rienäcker studied the electrometric titration of salts of copper, silver, and gold with chromous chloride. According to E. M. Péligot, gold is precipitated from a soln. of *gold trichloride*, and the reaction is accompanied by an evolution of hydrogen; and *mercuric chloride* furnishes mercurous chloride. H. Brintzinger and F. Oschatz followed the electrometric titration of *molybdic acid* with chromous chloride down to the formation of tervalent molybdenum; and H. Brintzinger and F. Rodis, alloys of tin and antimony, copper and tin, and bismuth and tin. N. H. Furman titrated chromous salts with soln. of ceric sulphate. E. M. Péligot found that *tungstic acid* is reduced to the blue lower oxide; and H. Löwel obtained tin from a soln. of *stannous chloride*. E. Zinth and G. Rienäcker studied the electrometric titration of salts of mercury, bismuth, and iron with chromous chloride.

As indicated above, H. Moissan obtained what he regarded as a *hexahydrate* by evaporating aq. soln. of chromous chloride; but A. Recoura, G. Baugé, and W. A. Knight and E. M. Rich showed that the product is the tetrahydrate, $CrCl_2.4H_2O$, and they recommended the following mode of preparation:

> Chromous acetate is dissolved in conc. hydrochloric acid in vacuo, and the clear soln. is boiled down to dryness. If this distillation is too prolonged, or if it is interrupted overnight, the dark green isomeride is usually formed, whilst if the temp. rises above 51° after crystals have begun to appear, the product is pale blue or light green or white, but these are varieties of the blue isomeride, and are finally converted into the stable dark blue hydrate in presence of cold water. The blue crystals are washed by repeated decantation with pure acetone, and the final drying carried out with ether.

The blue crystals of the tetrahydrate readily absorb oxygen from air to form a greenish-black oxychloride. W. A. Knight and E. M. Rich showed that the blue crystals prepared in this way appear to undergo no alteration when left for many months, but, in spite of the high degree of purity of this chromous chloride (especially when it has been reprecipitated from sat. soln. by conc. hydrochloric acid), its soln., on exposure to the air, has a markedly disagreeable odour. Water, not hydrogen chloride, is evolved when the hydrated salt is heated in vacuo at 180°. T. Döring found that the transformation of soln. of chromous chloride into chromic chloride is catalytically accelerated by platinum, gold, silicic acid, etc. J. W. McBain also studied the catalytic decomposition in the presence of colloidal platinum. M. Prud'homme showed that chromous chloride is green in hot, conc. soln., although its cold, dil. soln. is blue, and hence, by analogy with the chromic salt, he inferred that two isomeric forms exist in aq. soln. J. W. McBain isolated a dark green chromous chloride which gave a green soln. with water, but the soln. soon became azure-blue. The change from a green to a blue soln. occupies only a few seconds in neutral soln. at ordinary temp., but in acidic soln. the change is so retarded that it may require weeks for its completion. If the change from blue to green were due to a partial hydrolysis resulting in the formation of a green $Cr(OH)^{\cdot}$-cation, then it is difficult to explain M. Prud'homme's observation that conc. hydrochloric acid favours the formation of the green colour. The assumption that the change is due to a partial dissociation resulting in the formation of stable $CrCl^{\cdot}$-cation which colours the liquid green is supported by W. A. Knight and E. M. Rich's observation that the presence of a large proportion of another chloride favours the green colour. Observations on the f.p. of the green and blue soln. show that it is probable that the blue soln. furnishes three ions: $CrCl_2 \rightleftharpoons Cr^{\cdot\cdot} + 2Cl'$, while the green soln., being less ionized, furnishes two ions: $CrCl_2 \rightleftharpoons CrCl^{\cdot} + Cl'$.

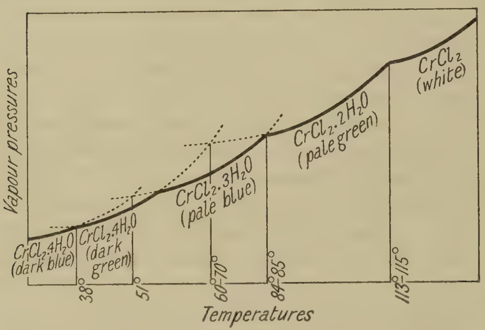


FIG. 73.—Diagrammatic Relation between Temperature and, say, Vapour Pressure of the Hydrated Chromous Chlorides.

W. A. Knight and E. M. Rich showed that if water be pumped from the tetrahydrate at 50°, a mixture of pale blue *trihydrate*, $CrCl_2.3H_2O$, and light green dihydrate is formed, but when water is added, the light green hydrate becomes pale blue trihydrate. The flask and contents are then heated to 51°, and the pale blue trihydrate is quickly dried at ordinary temp. by evacuation through a phosphorus pentoxide tube. The light green *dihydrate*, $CrCl_2.2H_2O$, is formed when water is pumped from the tetrahydrate between 70° and 80°; evacuation at 100° has no further effect. The dark blue tetrahydrate is the stable form up to 38°, when it passes into the dark green tetrahydrate; but if the dark green tetrahydrate does not appear, the dark blue modification is stable up to 51°, at which it passes into the pale blue trihydrate; the dark green tetrahydrate is stable between 38° and 60°–70°, when it forms the light green dihydrate. The pale blue trihydrate is converted into the light green dihydrate at 84°–86°, and this, in turn, becomes the white anhydrous chloride at 113°–115°. Fig. 73 represents the relationship between, say, the vap. press. or the conc. of sat. soln. and temp. The metastable regions are represented by dotted lines. The observed vap. press., p mm., with sat. soln. were

	25°	35°	45°	48°	49°	50°	55°	60°	65°
p . .	2·9	8·0	19·0	25·0	27·6	28·8	39·7	56·0	78·4
	$CrCl_2.4H_2O$					$CrCl_2.3H_2O$			

There is a definite break in the curve at 49°, which is close to the 51° obtained by observations on the change of colour.

L. N. Vauquelin [2] evaporated a soln. of chromic oxide in hydrochloric acid to dryness and heated the product to expel the last traces of water. H. Rose said that the last traces of water cannot be expelled without forming chromic oxide which colours the mass green. J. J. Berzelius, and H. F. Gaultier de Claubry heated the residue to a high temp. when a large proportion sublimed as **chromic chloride,** or **chromium trichloride,** $CrCl_3$. H. Rose, and H. Löwel obtained the anhydrous chloride by heating the hydrated salt, obtained by evaporating an aq. soln. of the chloride, in a current of dry chlorine so that chromium trichloride sublimes. F. Wöhler found that heated chromium burns in chlorine forming violet chromium trichloride. H. Moissan said that the reaction occurs at 600°. J. Y. Johnson heated ferrochromium in chlorine gas with or without a reducing agent like carbon monoxide. Heat is required to start the reaction, but thereafter the temp. is controlled by varying the amount of chlorine so that iron chloride is sublimed. F. Wöhler, and C. E. Ufer also obtained this chloride by passing dry chlorine over an intimate mixture of chromic oxide and carbon. H. Moissan heated to 400° chromic oxide, which had not been previously calcined, in dry chlorine gas, and A. Vosmär applied the reaction to the opening up of ferrochromium for analysis. F. M. Jackson heated ferrochrome in chlorine at above 350° to volatilize the ferric chloride, and then to 650° to produce chromic chloride. R. D. Hall obtained the trichloride by heating chromic oxide in a current of sulphur monochloride vapour; C. Matignon and F. Bourion used a mixture of sulphur monochloride and chlorine with the chromic oxide at 400°; F. Bourion preferred sulphur dichloride. J. R. Mourelo considered this to be the best mode of preparation. E. Demarçay passed carbon tetrachloride vapour over chromic oxide to obtain chromic chloride—P. Camboulives recommended a temp. of 580°. G. Rauter observed that when chromium trioxide or a chromate is heated in the vapour of silicon tetrachloride, chromic chloride is formed; and A. Michaelis found that it is formed by the action of phosphorus trichloride on chromyl chloride. H. Quantin prepared chromic chloride by heating chromyl chloride in a current of carbon monoxide, or of carbon tetrachloride; and M. Prud'homme worked with the materials in a sealed tube at 200°. F. P. Venable and D. H. Jackson found that the chlorination of chromic oxide with a mixture of chlorine and carbon monoxide starts at 625°. P. Curie passed the vapour of carbon disulphide mixed with hydrogen chloride over heated chromic oxide; and J. J. Berzelius, C. E. Ufer, F. Serena, and L. R. von Fellenberg passed chlorine over heated chromium sulphide.

Chromic chloride, according to H. Rose, furnishes micaceous, puce or violet laminæ. Like talc, they leave a mark on the skin. The colour of chromic chloride becomes very much paler at liquid air temp. G. Natta found that chromic chloride crystallizes in the trigonal system—probably holohedral. The X-radiograms show that the unit cell has a side $a=4{\cdot}42$ A.; the axial ratio $a : c=1 : 1{\cdot}29$ or $1{\cdot}30$; and contains one mol. of $CrCl_3$ per unit cell; and the calculated sp. gr. is 2·71. On the other hand, N. Wooster found that the unit cell contains six molecules, the chlorine atoms being arranged in cubic close-packing, and the chromium atoms occupy octahedral positions. The parameter $a=6{\cdot}0$ A., and $c=17{\cdot}5$ A. A. Schafarik gave 3·03 for the sp. gr.; F. W. Clarke and J. P. Grabfield gave 2·757 at 15°/4°; and W. Biltz and E. Birk, 2·784 at 25°/4°. M. Crespi found the sp. gr. of the anhydrous salt heated at 100° in dry air is 2·916. It is difficult to dry the substance, and it absorbs water greedily. The absorption resembles the process of adsorption of gases by glass. The mol. vol. of the contained water increases with the quantity of water retained by the salt. L. F. Nilson and O. Pettersson found the *vapour density* (air unity) to be 6·13 at 1065°; 5·51 at 1191°; 5·42 at 1277°; 4·82 at 1347°; and 4·58 at 1350°–1400°, when the theoretical value for $CrCl_3$ is 5·478. Hence, the simple formula $CrCl_3$ represents the molecule in the state of vapour; above 1300°, dissociation sets in: $2CrCl_3 \rightleftharpoons 2CrCl_2+Cl_2$. A. Scott confirmed these results. P. Fireman and E. G. Porter said that the dissociation, indeed, can be detected at 355°, for when an inert gas is passed over the chloride at that temp. and then through a soln. of potassium iodide, iodine is set free by the chlorine. F. Ephraim gave for the dissociation press., *p*, for $2CrCl_3 \rightleftharpoons 2CrCl_2 + Cl_2$, 205 mm. at 885°; 209 mm. at 902°; 415 mm. at 920°; 535 mm. at 930°; and 605 mm. at 933°. The results, however, are complicated by the volatility of the chromium chloride. H. Kopp gave 0·143 for the *specific heat.* K. Jellinek and R. Koop gave for the *vapour pressure:*

	700°	800°	900°	1000°
P . .	0·0187	0·0618	0·1845	0·366 atm.

A. Recoura gave for the heat of formation: $CrCl_{2soln.} + Cl_{gas} = CrCl_{3soln.} + 56·7$ Cals. K. Jellinek and R. Koop gave for the reaction $2CrCl_2 + Cl_2 = 2CrCl_3 + 66·95$ Cals.; and for $Cr + 1·5Cl_2 = CrCl_3$, 110·18 Cals. O. Stelling studied the X-ray absorption spectrum; C. P. Snow and F. I. G. Rawlins, the colour; and P. Krishnamurti, the Roman effect. W. Hampe found that the *electrical conductivity* of the trichloride is very small. T. Peczalsky and J. Cichocky studied the effect of chromic chloride on the thermionic emission of copper. S. Meyer gave 34×10^{-6} mass units for the *magnetic susceptibility* of chromic chloride at 18°; E. Feytis gave $44·1 \times 10^{-6}$ mass units; and for the atomic magnetism, R. H. Weber gave 0·00631. H. R. Woltjer, and H. R. Woltjer and H. K. Onnes observed that the susceptibility of chromic chloride decreases with the strength of the magnetic field at the temp. of liquid hydrogen; and for a given field strength, the susceptibility increases with falling temp. The observed data down to 64° K. follow the relation $\chi(T\text{-}32·5)$=constant, where χ denotes the susceptibility and T the absolute temp. For the aq. soln., G. Quincke gave the magnetic susceptibility 40×10^{-6} mass unit at 19°; S. Ishiwara gave $44·3 \times 10^{-6}$ mass unit at 18·5°; and G. Jäger and S. Meyer, 47×10^{-6} mass unit at 19°.

A. Moberg, and E. M. Péligot observed that when *hydrogen* is passed over the heated chromic chloride, chromous chloride is formed, and J. J. Berzelius, and A. Moberg noted that at a higher temp. chromium is produced; K. Jellinek and R. Koop, that the reduction of chromic chloride by hydrogen proceeds $2CrCl_3 + H_2 \rightleftharpoons 2CrCl_2 + 2HCl$ between 416° and 510°, and $CrCl_2 + H_2 \rightleftharpoons 2HCl + Cr$ between 1021° and 1192°. V. N. Ipatieff and B. A. Mouromtseff found that a soln. of the chloride is reduced by hydrogen at 200 atm. press. H. Rose observed that when heated in *air,* chromic chloride is quietly reduced to the oxide. J. Y. Johnson converted the anhydrous salt into the hydrate without the aid of a reducing agent as catalyst by exposing an aq. suspension to the action of a cathodically polarized conductor, *e.g.* in a lead-lined iron vessel having a chromium anode and using a very low current density. The heat generated in the process enables a highly conc. soln. to be produced, which is filtered while hot and solidifies on cooling. H. Kunheim said that when heated in *water vapour,* chromic chromate is formed; and F. Bourion found that when heated in *oxygen* mixed with water vapour, chromic oxide is produced. For the solubility in water, *vide infra.* R. Schwarz and G. Meyer observed that anhydrous chromic chloride does not take up *hydrogen chloride.* A. Recoura found that if hydrogen chloride be passed for some days into a soln. of chromic chloride, the liquid gradually becomes brown or brownish-red, owing to the formation of a **chromic hydrochloride.** If ether be added, a green, unstable precipitate approximating $CrCl_3.HCl$ is formed. A. W. Cronander obtained a blue complex **chromic phosphoctochloride,** $CrCl_3PCl_5$, by the action of *phosphorus pentachloride* on chromic or chromyl chloride in a sealed tube at 150°. R. F. Weinland and C. Feige, and P. Pfeiffer prepared a complex with *antimony pentachloride,* namely, **chromium antimonioctochloride,** $CrCl_3.SbCl_5.10H_2O$, in green leaflets, and **chromium triantimoniododecachloride,** $CrCl_3.3SbCl_3.13H_2O$, in violet-grey needles. R. F. Weinland and H. Schmid obtained $Cr[SbCl_6]_3.15H_2O$, and also $[SbCl_6].CrCl_2.10H_2O$—*vide* antimony pentachloride, **9.** 52, 18. H. Rose said that puce-coloured chromic chloride is extraordinarily resistant towards acids. According to L. R. von Fellenberg, boiling *hydrochloric*, or *nitric acid*, or *aqua regia* does not act on the chloride, but N. Bunge found that if a little sodium amalgam be added to dil. hydrochloric acid in which the trichloride is suspended, a green soln. and some chromium amalgam are formed. H. Rose observed that conc. *sulphuric acid* can be distilled from the puce-coloured chloride, but J. Pelouze added that with hot, conc. sulphuric acid, chlorine is slowly given off, leaving behind a green mass miscible with water. Molten *sulphur* was found by J. L. Lassaigne, and J. J. Berzelius, to furnish chromium sulphide ; J. von Liebig noted that when heated in *hydrogen sulphide*, chromium sulphide is formed ; H. Moissan said that *ammonium chloride* at a red-heat forms chromous chloride ; A. Schrötter, that *ammonia* converts it into nitride. J. Persoz studied the action on chromic chloride. Neither aq. ammonia nor ammonia gas acts on violet chromic trichloride, but W. R. Lang and C. M. Carson found that the puce trichloride reacts with liquid ammonia forming a yellow powder from which water extracts **chromic hexamminochloride,** $CrCl_3.6NH_3.H_2O$, and also **chromic pentamminochloride,** $CrCl_3.5NH_3$; while W. R. Lang and E. H. Jolliffe obtained with *methylamine* the complex **chromic pentamethylaminochloride,** $CrCl_3.5(CH_3)NH_2$; and with *ethylamine*, **chromic pentaethylaminochloride,** $CrCl_3.5(C_2H_5)NH_2.H_2O$, whilst, at 60°, it forms **chromic tetraethylaminochloride,** $CrCl_3.4(C_2H_5)NH_2.H_2O$; *ethylenediamine* forms **chromic tetraethylenediaminochloride,** $CrCl_3.4C_2H_4(NH_2)_2.H_2O$; while *dimethylamine, diethylamine, trimethylamine, triethylamine, aniline, methylaniline*, and *dimethylaniline* have no action on chromic chloride. P. Pfeiffer obtained a salt with *pyridine*, namely, **chromic tripyridinochloride,** $CrCl_3.3C_5H_5N$—*vide infra*, ammines. G. Fuseya and K. Murata observed the complexes are formed with *glycine ;* and H. Farl, with pyridine and chromic dichloroethylate. G. M. Bennett and E. E. Turner studied the reaction with *magnesium phenyl bromides :* $2CrCl_3+2(C_6H_5)MgBr=C_6H_5.C_6H_5+2CrCl_2+MgCl_2+MgBr_2$, etc. F. Hein obtained chromium phenyl bromide, $Cr(C_6H_5)_5Br$, as a product of this reaction. H. Rose found that *phosphine* produces the phosphide. I. Koppel said that the puce-coloured, anhydrous chloride does not dissolve in *ethyl alcohol*, but it does so if a piece of magnesium, zinc, or chromium be present, or if a trace of chromous acetate be added. According to L. C. A. Barreswill, when chromic chloride and alcohol are heated in a sealed tube, ethyl chloride is formed. F. Pintus, and I. Koppel obtained **chromium alcoholatochloride,** $CrCl_3.3C_2H_5OH$, in red needles—*vide infra*, ammines. P. A. Thiessen and B. Kandelaky examined these salts. P. Rohland said that puce-coloured chromic chloride is practically insoluble in absolute ethyl alcohol, *methyl alcohol, acetaldehyde*, and in *ether.* W. Eidmann found it to be insoluble in *acetone ;* and H. Arctowsky, in *carbon disulphide.* A. Naumann said that the puce-coloured chloride is sparingly soluble in *methyl acetate ;* and that the yellow form is slightly soluble in *benzonitrile.* L. Hackspill found that *calcium* reduces heated chromic chloride to chromium ; F. Wöhler, that zinc, in molten potassium chloride, reduces it to chromium ; L. R. von Fellenberg, and H. Rose said that the puce-coloured chloride is insoluble in dil. alkali-lye, and that it is decomposed by boiling conc. soln. of *alkali hydroxides and carbonates ;* A. Geuther, that it reacts with chromium trioxide: $3CrO_3+2CrCl_3=Cr_2O_3+3CrO_2Cl_2$; and with molten *potassium dichromate :* $3K_2Cr_2O_7+2CrCl_3=Cr_2O_3+6KCrO_3Cl$. F. Wöhler obtained crystalline chromic oxide by fusing the trichloride with *sodium carbonate* and ammonium chloride.

According to N. Bunge, C. W. Vincent, and Z. Roussin, a slightly acidified soln. of chromic chloride or other chromium salt yields with **sodium-amalgam** an easily decomposable chromium amalgam. A. Commaille observed that **magnesium** precipitates only hydrated chromic oxide from a soln. of chromous or chromic chloride. K. Someya found that soln. of chromic salts are quantitatively reduced to chromous salts by **zinc-amalgam** or **lead-amalgam;** and C. Boulanger studied the reduction with **zinc** and with **aluminium**. According to T. Peczalsky, when a **copper** rod has its lower half surrounded by chromic chloride, cementation is produced throughout its length, specially on the portion in contact with the salt. Metallic chromium was deposited on the rest of the rod, whilst rhombohedric copper crystals were found in the salt. If the rod was contained in exhausted "pyrex" tubes, surrounded by chlorides of copper, nickel, or chromium, deposits of copper were found to have penetrated the glass after 5–10 hrs. at 600°–800°.

H. Rose said that the anhydrous, puce-coloured chromic chloride is insoluble in cold water; and E. M. Péligot, that it is insoluble in boiling water. J. Pelouze added that it is very slowly soluble in cold water, but water at 150°–200° forms a deep green soln. H. Moissan also obtained an aq. soln. by heating the chloride with water in a sealed tube at 180°. According to E. M. Péligot, while chromic chloride is insoluble in cold water, yet, when in contact with chromous chloride, it dissolves with ease, heat being evolved, and a green soln. formed. The soln. has all the characteristics of chromic salts. A very small quantity, less than 0·000001 per cent. of chromous chloride, suffices to render chromic chloride soluble.

A. Moberg, and K. Drucker found that the dissolution of chromic chloride is facilitated by the presence of dil. acid and zinc; K. Drucker, aluminium, ferrous oxalate; a soln. of copper in cuprous sulphate, a soln. of arsenious acid and sodium hydrocarbonate or hydrogen in the presence of colloidal platinum at ordinary temp.; J. Pelouze, stannous, ferrous, or cuprous chloride, or sodium thiosulphate; V. A. Jacquelin, titanous chloride, or sulphur dioxide; H. Moissan, chromous bromide or iodide; and P. Rohland, hydrogen at 90°; and the following metals in contact with the chromic chloride have a decreasing order of activity in facilitating the dissolution of the salt: potassium, sodium, magnesium, aluminium, zinc, cadmium, tin, iron, nickel, lead, antimony, bismuth, copper, mercury, and silver—while platinum and gold are inactive. M. Bauck noticed that a piece of chromic chloride deliquescing on tinfoil forms a green spot presumably owing to the formation of a little chromous chloride by the reducing action of the tin. P. Rohland found that in methyl or ethyl alcohol, or acetone soln., the activity of chromous chloride in promoting the dissolution is less than in aq. soln.

E. M. Péligot, and J. J. Berzelius said that the chromous chloride acts as a contact catalyst; and L. C. A. Barreswill assumed that the chromous chloride forms with violet chromic chloride a double salt which decomposes into chromous chloride and a green soluble chromic chloride. H. Löwel supposed that the chromous chloride reduces the violet chromic chloride and at the same time is transformed into soluble chromic chloride, and the reaction continues anew. A. Recoura's hypothesis was somewhat similar to this. P. Rohland said that the action is not catalytic, but that it favours the dissolution of the chromic chloride by its reducing action. A considerable proportion of stannous chloride is required to do this work, and that indicates that the action is not a characteristic of catalyzed reactions. K. Drucker measured the rates of dissolution in the presence of various reducing agents—*vide supra.* He found that the rate is dependent upon (i) the nature of the reducing agent, (ii) its reduction-potential, increasing and decreasing with this, and (iii) its absolute conc. In the presence of a sparingly soluble reducing agent, the dissolution of the chromic chloride takes place provided that the agent is also present in the solid state. The function of the reducing agent does not appear to be entirely catalytic, but a reaction takes place between this and the chromic chloride. The dissolution is probably preceded by a slight reduction to chromous chloride, the catalytic influence of which is very great; only a small quantity of this can, however, be formed, since its potential in soln. of appreciable conc. is greater than that of hydrogen, whilst the potential in the soln. cannot rise above that of the reducing agent present. It has not been proved that the catalytic influence is wholly due to chromous chloride. E. Hein and co-workers studied some complexes with organic radicles.

The hydrated chromic chlorides are perhaps the most peculiar hydrated salts in inorganic chemistry. There are one tetrahydrate, three isomeric hexahydrates —violet, pale green, and dark green—and one decahydrate; and, as indicated below, the dehydration of the dark green hexahydrate furnishes a *hemihydrate*, $CrCl_3.\frac{1}{2}H_2O$, and a *hemitrihydrate*, $CrCl_3.1\frac{1}{2}H_2O$.

The tetrahydrate, $CrCl_3.4H_2O$.—L. Godefroy[3] prepared this salt by allowing the dark green hexahydrate to stand over conc. sulphuric acid in vacuo. The pale green powder readily takes up 2 mols. of water to form the hexahydrate, with the evolution of heat—according to G. O. Higley—eq. to 83·96 Cals. A. Werner and A. Gubser showed that the tetrahydrate can also form double salts with 2 mols. of, say, alkali chloride. The aq. soln. of the tetrahydrate is identical with the aq. soln. of the dark green hexahydrate. A. E. Lindh studied the X-ray absorption spectrum. The mol. conductivity of the aq. soln., rapidly determined at 0°, is 49 at a dilution v=125—the conductivity increases to the value for the dark green hexahydrate after it has stood for some time. The arguments with respect to the constitution of the dark green hexahydrate (*q.v.*) are applicable to this salt. The 4 mols. of water are considered to be constitutional because they are not removed by drying. This means that the tetrahydrate can be regarded as **chromic dichlorotetraquochloride,** $Cr[Cl_2(H_2O)_4]Cl$.

The dark green hexahydrate, $CrCl_3.6H_2O$.—This salt was prepared by A. Moberg, and E. M. Péligot by evaporating the green soln. in vacuo; the green soln. used by the latter was obtained by dissolving the puce-coloured anhydrous chloride in water containing a trace of chromous chloride. P. Rohland prepared the salt in a similar way. H. Rose obtained the green soln. by boiling chromic acid in hydrochloric acid, or by dissolving hydrated chromic oxide in that acid; E. M. Péligot, by evaporating a mixture of lead chromate and hydrochloric acid, and extracting the chromic chloride with alcohol, or from the clear soln. obtained by digesting lead chromate with alcohol and hydrochloric acid; L. Godefroy sat. with chlorine a soln. of 3 parts of potassium dichromate in 7 parts of alcohol. The soln. was filtered through cotton-wool, and the filtrate distilled until it separated into two layers. On cooling, the green lower layer solidified to a mass of crystals which were purified by recrystallization from a small quantity of water. The crystals thus obtained are thin lozenge-shaped lamellæ which readily give off some of their water, but can be preserved in a closed vessel. A. Recoura, N. Bjerrum, and A. Werner and A. Gubser passed hydrogen chloride into a sat. soln. of chromic chloride prepared from chromium trioxide and hydrochloric acid, when crystals which have been variously described as green, or emerald-green needles or plates were obtained; R. F. Weinland and A. Koch, and A. Johnsen said that the crystals are six-sided, biaxial, monoclinic or triclinic plates; and J. Olie described them as doubly refracting, rhombic or pseudohexagonal plates. W. Biltz and E. Birk gave 1·835 for the sp. gr. at 25°/4°; and 145·2 for the mol. vol. The hygroscopic crystals were said by A. Werner and A. Gubser to have an intensely sweet taste. The analyses of A. Moberg, and A. Recoura gave rather different values for the amount of water of crystallization, but the analyses of E. M. Péligot, L. Godefroy, and A. Werner and A. Gubser agree with the formula $CrCl_3.6H_2O$. A. Werner and A. Gubser found that 2 mols. of water are readily withdrawn when the salt is confined over sulphuric acid in vacuo, but no more water is lost. On the other hand, J. Olie said that more than this amount of water can be removed because after long standing over sulphuric acid in vacuo at 15°, the surface of the salt becomes pale red. When heated for 6 hrs. at 100°, rather more than 4 mols. of water are expelled. The product is dark violet; it readily absorbs water from the atm.; and forms a soln. almost identical in appearance and behaviour with the original green salt. Some hydrogen chloride, however, was also given off under these conditions. N. Bjerrum observed that when the salt is kept for 4 months over phosphorus pentoxide, under 1 mm. press., there remains the red hemitrihydrate, $CrCl_3.1\frac{1}{2}H_2O$, which forms a yellowish-green soln. with water, changing to the violet-blue colour

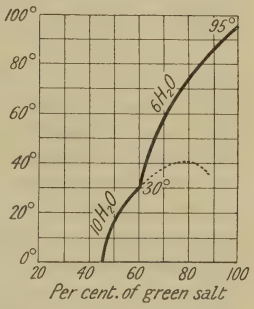


Fig. 74.—Solubility of Green Chromic Chloride in Water.

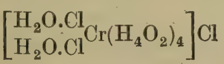
of the aq. soln. of green chromic chloride. J. Olie found that the natural m.p. of the salt—with 36 per cent. of the violet isomer—is 83°, and the true m.p. is over 90°—*cf.* Fig. 76; the salt can be heated slowly to 100° in vacuo without melting. J. Olie gave 2·66 Cals. for the heat of transformation to the violet isomer. H. de Bois and G. J. Elias measured the effect of temp., and of a magnetic field on the absorption spectrum of solid chromic chloride. The electrical conductivity of the soln. of the hemitrihydrate is at first less than that of the soln. of the hexahydrate, but it increases rapidly after a few minutes. If the green hexahydrate be heated very slowly to 155°, in a current of hydrogen chloride, there remains the hemihydrate, $CrCl_3.\frac{1}{2}H_2O$, as red powder. A. Recoura found that the green hexahydrate is freely soluble in water, so that at 15° the sat. soln. has 56·6 per cent. of the salt. J. Olie inferred that at 25° a sat. soln. has 50 per cent. of the green salt, but in the process of dissolution some violet salt is formed, and the change from the green to the violet salt (*vide infra*) goes on slowly until equilibrium is attained in about 10 days; this is accompanied by an apparent increase in the solubility of the salt, because the violet salt is rather more soluble than the dark green salt. Thus, at 25°, the percentage solubility, *S*, and the percentage proportions of dark green and violet salts in soln., are:

Time .	0·25	0·5	4·0	24	48	154	456 hrs.
S .	58·36	59·39	63·27	68·50	68·42	69·01	68·58 per cent.
Green .	91·70	87·43	75·20	62·36	59·10	57·16	57·38 ,,
Violet .	8·30	12·57	24·80	37·64	40·90	42·84	42·62 ,,

J. Olie also observed that the formation of the decahydrate introduces a complication, because there is a transition point near 30° when the system contains about 32 per cent. of the violet salt and 68 per cent. of the green salt. If a soln. sat. at a temp. below 32° is cooled, only the decahydrate separates out; but if sat. above 32°, both hexahydrate and decahydrate separate on cooling. A. Werner and A. Gubser also found that at room temp. the decahydrate changes to its equilibrium form very slowly. J. Olie represented his results by a diagram resembling Fig. 74. E. N. Gapon studied the speed of hydration and dehydration and of the passage ot the green to the violet hydrate; and the mechanism of the charge, by L. Meunier and M. Lesbre. A. Recoura gave —0·04 Cal. for the heat of soln. of a mol of the green hexahydrate in 150 mols of water, but, according to J. Olie, this datum does not represent the heat of soln. of the green hexahydrate, but rather the heat of hydration to the decahydrate, and the heat of soln. of the decahydrate. O. Stelling studied the X-ray spectrum. E. Feytis observed that the magnetic susceptibility $23{\cdot}0 \times 10^{-6}$ mass unit is very little different from the value for the violet salt. R. H. Weber made observations on this subject. E. Feytis gave for the mol. susceptibility 6179×10^{-6}, and J. B. Elias, 6100×10^{-6}. N. Bjerrum found that the dark green hexahydrate is soluble in fuming hydrochloric acid; A. Werner and A. Gubser, that it is freely soluble in alcohol, sparingly soluble in acetone, and insoluble in ether; and P. Rohland, that it is nearly insoluble in ether, and freely soluble in methyl and ethyl alcohols as well as in acetaldehyde. The salt is largely ionized in methyl alcoholic soln., but the mol. wt. is normal in ethyl alcohol and in acetone soln. The formation of the salt was also studied by L. Meunier and M. Lesbre. From the properties of the soln., indicated below, A. Werner and A. Gübser regarded the dark green hexahydrate as **dihydrated chromic dichlorotetraquochloride,** $[CrCl_2(H_2O)_4]Cl.2H_2O$, with 2 masked chlorine atoms; the hypothesis is based on the behaviour of the salt on drying; on treatment with silver nitrate; and on the electrical conductivity of aq. soln.—*vide infra.* They also represented it by the formula $[(H_2O.Cl)_2Cr(H_2O)_4]Cl$.

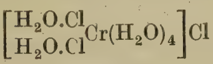
The pale green hexahydrate, $CrCl_3.6H_2O$.—This salt was prepared by N. Bjerrum by pouring a hydrochloric acid soln. of chromic chlorosulphate into ether sat. with hydrogen chloride; and by boiling a soln. of 13·4 grms. of chromic dichlorotetraquochloride in 18 grms. of water for 10 mins., then sat. the soln. at 8°–10° with hydrogen chloride ; the filtered liquid was then poured into 200 c.c. of ether sat. with hydrogen chloride at 10°, while hydrogen chloride is passing through the liquid. The salt separates out when the soln. is allowed to stand, and it is washed with ether sat. with hydrogen chloride. The pale green hexahydrate is supposed to be present in aq. soln. containing the other two chlorides, and is said to be a maximum when the green dichlorotetraquochloride is dissolved in its own weight of water, and the soln. boiled for 10 mins.—*vide infra.* G. O. Higley obtained it by heating the violet salt to 70° ; and by evaporating a soln. of the green chloride and hydrochloroplatinic acid, he obtained the salt $[Cr(H_4O_2)_5Cl]PtCl_6$. A. del Campo and co-workers obtained this salt by saturating with hydrogen chloride an aq. ethereal soln. of green chromic chlorosulphate, $[CrCl(H_2O)_5]SO_4.H_2O$. The pale green hexahydrate was also prepared by A. Werner and R. Huber, and by R. F. Weinland and T. Schumann. W. Biltz and E. Birk found the sp. gr. to be 1·760 at 25°/4°, and the mol. vol. 151·4. According to N. Bjerrum, the pale green, microcrystalline powder is very hygroscopic, and it slowly passes into the dark green salt. It is soluble in a mixture of equal vols. of fuming hydrochloric acid and ether forming a green soln., which, when poured into an excess of ether sat. with hydrogen chloride, deposits the pale green solid. The pale green hexahydrate forms a bluish-green soln. with water, and the colour slowly changes to bluish-violet ; it is soluble in alcohol, and in acetone. Conc. sulphuric acid precipitates from the aged aq. soln., $CrClSO_4.6H_2O$. This behaviour of the salt together with its behaviour towards silver nitrate, and the conductivity of its aq. soln., suggests that the salt is **hydrated chromic chloropentaquodichloride,** $[Cr(H_2O)_5Cl]Cl_2.H_2O$, with one masked chlorine atom.

The decahydrate, $CrCl_3.10H_2O$.—L. Godefroy prepared this salt by placing a sat. soln. of the dark green hexahydrate in vacuo for several days at a temp. below 6°. A. Werner and A. Gubser obtained it by cooling, by means of a freezing mixture, a soln. of the dark green hexahydrate in half its weight of water ; and J. Olie, by triturating the dark green hexahydrate with the theoretical proportion of water. L. Godefroy described the salt as forming green, triclinic crystals, which readily lose water. Over sulphuric acid, for example, they lose 4 mols. of water, and become opaque and friable. The salt melts slowly in its water of crystallization at a temp. above 6° or 7°. J. Olie found that when rapidly heated, the salt melts at 32°. This temp., however, is not a m.p., but rather a transition temp.—*vide* Fig. 74—A. Werner and A. Gubser found that the decahydrate is freely soluble in water, alcohol, and acetone. G. O. Higley found that the heat of soln. is zero ; but in conc. soln., J. Olie found that the heat of soln. is negative. N. Bjerrum's observations on the extinction coeff. of the soln. are summarized in Fig. 75. The mol. conductivity of a fresh $0·00988M$-soln. at 25° is 208·5 mhos, a value which is mean between those obtained for soln. of the dark green and the violet hexahydrates of the same conc. The hydrolysis constant, $K=8\times10^{-6}$ nearly, is about one-tenth the value for the violet salt. The conc. aq. soln., with conc. sulphuric acid, forms the chlorosulphate, $CrClSO_4.6H_2O$, or $[CrCl(H_2O)_5]SO_4.H_2O$. According to A. Werner and A. Gubser, the mol. conductivity, and the behaviour of the salt towards silver nitrate indicate that it contains two non-ionizable chlorine atoms ; and it behaves like **hexahydrated chromic dichlorotetraquochloride,** $[Cr(H_2O)_4.Cl_2]Cl.6H_2O$. Two of the ten mols. of water can be replaced by metal chlorides. It is assumed that four of the mols. of the hexahydrate are doubled. The tetrahydrate, dark green hexahydrate, and the decahydrate all give aq. soln. of identical properties ; and this when the soln. is freshly prepared before they have had time to undergo the slow changes indicated below. Consequently, deca-, hexa-, and tetra-hydrates are supposed to be similarly constituted : either $[Cr(H_2O)_4Cl_2]Cl$, $[Cr(H_2O)_4Cl_2]Cl.2H_2O$, and $[Cr(H_2O)_4Cl_2]Cl.6H_2O$, or else



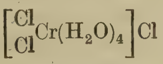
$$\left[\begin{matrix}H_2O.Cl\\H_2O.Cl\end{matrix}Cr(H_4O_2)_4\right]Cl$$

Decahydrate



$$\left[\begin{matrix}H_2O.Cl\\H_2O.Cl\end{matrix}Cr(H_2O)_4\right]Cl$$

Hexahydrate.



$$\left[\begin{matrix}Cl\\Cl\end{matrix}Cr(H_2O)_4\right]Cl$$

Tetrahydrate.

G. Quincke gave 1·2030 for the sp. gr. of a 20·8 per cent. soln. of $CrCl_3$ at 19°/4°. H. C. Jones and H. P. Bassett found the sp. gr. of soln. with M mols of the salt per litre at 18° to be :

M . .	0·05	0·1	0·2	0·4	0·6	0·9	1·5	2·25
Sp. gr. .	1·0099	1·0142	1·0258	1·0507	1·0773	1·1117	1·1806	1·2631

E. Moles and M. Crespi gave 1·802 for the sp. gr. and 147·5 for the mol. vol. According to W. Biltz and E. Birk, the mol. vol. of $[CrCl_2(H_2O)_4]Cl.2H_2O$ is 145·2 ; of $[Cr(H_2O)_6]Cl_3$, 148·1, and of $[CrCl(H_2O)_5]Cl_2.H_2O$, 151·4. The mol. vol. of the most stable of the chromic salts, the dark green dichlorotetra-aquochromic chloride dihydrate, $[CrCl_2(H_2O)_4]Cl.2H_2O$, is 145·2, that of the grey hexa-aquochromic chloride, $[Cr(H_2O)_6]Cl_3$, is 148·1, and that of the least stable, the light green monochloropenta-aquochromic chloride monohydrate, $[CrCl(H_2O)_5]Cl_2.H_2O$, is 151·4. The mol. vol. thus falls with increasing stability, as for organic isomerides, the difference for each pair being 2 per cent. The mol. vol. of chromous chloride hexahydrate is 129·6, and this corresponds with a volume of 14·5 for each mol. of water. The mol. vol. of the water in the chromic chloride hexahydrates are 14·7, 15·2 and 15·7, respectively, and the chromous chloride thus corresponds with the dark green chromic salt and may be formulated $[CrCl_2(H_2O)_4].2H_2O$. H. Lessheim and co-workers discussed the electronic structure. J. E. Howard and W. H. Patterson found that the effect of the dark green salt on the critical soln. temp. of binary mixtures of water with butyric acid, isobutyric acid, and phenol, and of ethyl alcohol and paraffin, is nearly twice that due to the violet salt for concentrations up to 0·05M ; above this conc., the difference becomes progressively smaller. H. C. Jones and H. P. Bassett found the lowering of the f.p. of aq. soln. of M mol of the salt per litre to be :

M .	0·05	0·1	0·2	0·4	9·6	0·9	1·5	2·25
F.p. .	−0·268°	−0·510°	−0·030°	−2·160°	−3·610°	−6·30°	−15·0°	−33·0°

Measurements were also made by G. Marchetti, and A. Werner and A. Gubser. The general results correspond with a mol. wt. nearly half the theoretical value 266·6. J. R. Partington and S. K. Tweedy observed that violet soln. of hexahydrated chromic chloride have a higher viscosity than analogous green soln., as would be anticipated from A. Werner's formulation of these salts. A. Recoura gave for the heat of the reaction $(CrCl_{3\text{green soln.}}.3NaOH_{\text{soln.}}) = 31·5$ Cals. at 10°, and the precipitated hydroxide dissolves in hydrochloric acid with the evolution of 20·7 Cals., or 20·6 Cals. according to E. Petersen ; the resulting soln. is blue. A. Piccini observed that the raising of the b.p. in methyl alcohol corresponds with a mol. wt. of about 50 ; in ethyl alcohol, 228 ; and in acetone, 271 ; the theoretical value is 266·6. F. Jost also obtained a mol. wt. of 33·2 in methyl alcohol. A. Recoura said that soln. appear green by reflected light, and red by transmitted light ; they found an absorption spectrum with a single green band ; a candle-flame viewed through such a soln. appears green ; but after the soln. has stood for 10 days a red band appears, and the flame finally appears to be reddish-violet. W. N. Hartley found that when anhydrous chromic chloride is dissolved in water, two kinds of salt are formed, one of which is precipitated by ammonium oxalate and the other not so. A soln. of the latter in thin layers at 20° shows a continuous

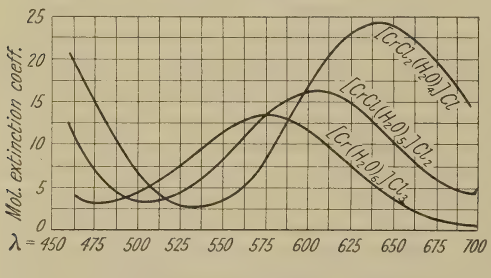


FIG. 75.—Molecular Extinction Coefficients of Solutions of the Chromic Chlorides for Light of Different Wave-lengths.

spectrum up to about λ=500 when bands appear at λ=704 to 685, and at λ=673 to 538. At 100°, the soln. is opaque. Observations were made by J. Formanek, W. Lapraik, J. M. Hiebendaal, J. L. Soret, H. W. Vogel, G. Magnanini, O. Knoblauch, A. Étard, H. C. Jones and J. A. Anderson, and H. C. Jones and W. W. Strong. N. Bjerrum found for the three hexahydrated chromic chlorides the mol. extinction coeff. illustrated by Fig. 75 for wave-lengths ranging from λ=450 to 700. The mol. extinction coeff., k, is defined by $I_0=I_e^{kml}$, where I_0 is the intensity of the incident light, and I the intensity after traversing a layer, l cm. thick, of a soln. with M mols per litre. In an analogous way, A. Byk and H. Jaffe measured the limits of absorption for ultra-violet rays ranging from λ=440 to 220, and found for the green soln. of the chloride (eq. to 5 grms. of chrome-alum for 100 c.c.) an absorption band λ=490 to 409·1 ; and for violet soln. bands λ=433·1 to 400·0, and λ=400·0 to 385·5. H. W. Vogel measured the absorption spectrum of alcoholic soln. ; and O. Stelling, the X-ray spectrum ; H. C. Jones and W. W. Strong, the effect of the presence of various other salts in the soln. of chromic chloride. N. Bjerrum found the mol. electrical conductivity, μ mhos, of aq. soln. with M mols per litre to be :

M . . .	0·00322	0·01074	0·00334	0·00998	0·0307	0·008
μ . . .	103·1	97·9	88·6	83·0	79·5	49·0

Observations were also made by A. Werner and A. Gubser, H. C. Jones and H. P. Bassett, H. C. Jones and C. A. Jacobsen, and A. B. Lamb. According to A. W. Speransky, the mol. conductivity of the soln. of the dark green salt, is about one-third of that of the violet salt. This, said A. Werner and A. Gubser, shows that a smaller proportion of ions is formed by the ionization of the salt, so that while the violet salt furnishes four ions per mol, the dark green salt yields only 2 ions. As the soln. of the green salt is allowed to stand, the ionization proceeds further, owing to the partial transformation of the green into the violet salt—*vide infra.* F. Jost gave for the mol. conductivity of soln. of the green salt in methyl alcohol, at room temp. :

M . . .	11·55	15·48	28·7	55·5	129·9
μ . . .	43·5	46·5	52·6	59·0	64·2 mhos.

H. C. Jones calculated for the percentage degree of ionization, α, and gave for the number of mols of water, H, in combination with a mol of the salt for soln. with M mols of salt per litre :

M . .	0·05	0·1	0·3	0·6	0·9	1·5	2·0	2·25
μ . .	52·7	46·9	38·1	31·2	25·6	16·9	11·6	9·6
H . .	117·9	66·6	42·5	39·2	31·8	26·0	22·1	20·2

L. G. Winston and H. C. Jones gave for the conductivity, λ, and the computed percentage ionization, α :

v	. .	4	8	32	128	512	1024	2048	4096
λ	0° .	86·30	104·53	130·03	162·34	188·46	200·21	214·48	229·73
	25° .	153·32	184·18	245·00	313·45	372·34	403·58	434·36	467·61
	35° .	199·10	243·55	319·15	393·62	465·10	504·31	543·02	586·16
α	0° .	37·6	45·5	56·6	70·7	82·1	87·2	93·3	100·0
	25° .	32·8	39·4	52·4	67·0	79·6	86·3	92·9	100·0
	35° .	34·3	42·0	55·0	67·9	80·2	86·9	93·6	100·0

H. M. Vernon estimated the degree of ionization from the colour of the soln. K. Hopfgartner's study of the transport numbers also led him to assume that the chromic ion is surrounded by a fairly large water sheath. F. L. S. Jones investigated the formation of complex anions in aq. soln.—*vide infra,* chromic sulphate. T. Murayasu studied the conductivity in soln. of the salt in glycine. N. Demassieux and J. Heyrovsky found that the polarization curve shows breaks at 0·7 and 1·35 volts, indicating that the electrochemical reduction occurs in two stages : $\mathrm{Cr}^{\cdot\cdot\cdot}\rightarrow\mathrm{Cr}^{\cdot\cdot}$, and $\mathrm{Cr}^{\cdot\cdot\cdot}\rightarrow\mathrm{Cr}$. The presence of an acid does not exert any influence on the deposition potential, and this is taken to mean that H˙-ions do not enter into the electrolytic process. It is also thought that the observations agree with the assumption that in conc. soln. the green chloride, $[CrCl_2(H_2O)_4]Cl.2H_2O$, is present; and that in dil. soln. the violet form, $[Cr(H_2O)_6]Cl_2$, predominates; and that it is easier to reduce the green complex than is the case with the violet.

According to E. Wiedemann, the atomic magnetism of chromium is about 42, when that of iron in ferric chloride is 42; and the result is independent of the anion associated with the chromium. Similar results were obtained by G. Jäger and S. Meyer. Observations on the subject were also made by E. Feytis, and R. H. Weber. E. Feytis gave for the mol. susceptibility 6181×10^{-6}; J. B. Elias, 5920×10^{-6}; and L. A. Welo found the susceptibility to be $22·6\times10^{-6}$ mass unit.

The co-ordination theory of the constitution of the hydrated chromic chlorides, said I. Koppel, *findet ihre stärkste Stütze in dem verschiedenen Verhalten der Chloridlösungen bei der Fällüng mit Silberion;* and A. B. Lamb and G. R. Fonda added that the application of the theory to the hydrated chromic chlorides is "perhaps the most striking exemplification of A. Werner's theory of molecular structure." The evidence lacks that decisive proof which would make the alternative hypotheses —*e.g.* the hydrolysis theory of their constitution—untenable. E. M. Péligot, and S. M. Jörgensen found that in the soln. of the dark green chloride two-thirds of the total chlorine is precipitated as silver chloride from newly prepared soln.; G. N. Wyrouboff said that five-sixths is so precipitated; while A. Werner and A. Gubser observed that at 0°, about one-third of the chloride is so precipitated—actually the amounts precipitated were rather greater than one-third. If the soln. are allowed to stand in contact with the silver salt, all the chlorine is ultimately precipitated as chloride. R. F. Weinland and A. Koch then showed that, using various silver salts as precipitants in the presence and in the absence of free acids, the proportion of chlorine precipitated depends on the nature and quantity of the particular silver salt employed. In the absence of acids, all the silver salts precipitated at least two-thirds of the chlorine as chloride; the presence of nitric acid diminished the proportion of precipitable chlorine; whereas silver salts of the weak acids—*e.g.* acetic, lactic, nitric or sulphuric acid—immediately precipitated all the chlorine. Silver salts of the strong acids—*e.g.* nitric, chloric, perchloric, or permanganic acid—did not precipitate all the chlorine as chloride, and the presence of strong acids suppressed the precipitation even more. A. Piccini also found that silver fluoride, like silver acetate, precipitated all the chlorine as chloride. He also found that a soln. of the dark green hexahydrate in ethyl alcohol or acetone gives up all its chlorine to an alcohol or acetone soln. of silver nitrate, whereas, with methyl alcohol soln., the results approximate to those obtained with water. J. Olie pointed out that R. F. Weinland and A. Koch used at least 3 eq. of silver salts and found at least two-thirds of the chlorine was precipitated; and he obtained similar results even with only 2·11 eq. of silver salt. J. Olie showed that the reaction $[CrCl_2(H_2O)_4]Cl.2H_2O \rightarrow [Cr(H_2O)_6]Cl_3$ is retarded or paralyzed by strong acids or H˙-ions; and he explained the fact that whilst the silver salts of strong acids precipitate only part of the chlorine, and silver salts of the weak acids precipitate nearly all the chlorine, owing to the removal of H˙-ions by the silver salts of the weak acids. The action of neutral salts, such as sodium and ammonium nitrates on precipitation by silver nitrate, is slight with small concentration, but a large amount of these salts greatly increases the proportion of chlorine thrown down. Strong acid at first cause a decrease in the proportion of chlorine precipitated until in certain concentrations only one eq. is affected; more conc. soln. cause an increase in the amount precipitated. Weak acids have a much smaller effect. The great effects of strong acids and neutral salts when present in considerable concentration is attributed to a direct exchange of the chlorine in the positive nucleus for other groups. A. B. Lamb said that the retarding action of the H˙-ions on the isomeric change can be explained by assuming that one stage of the process involves the hydrolysis of the dark green chromic salt, say, $[CrCl_2(H_2O)_4]+Cl'+OH'+H^{\cdot}$

$\rightleftharpoons[CrCl_2(H_2O)_4]OH+H^{\cdot}+Cl'$. The chlorine in the central group may also be displaced by an analogous process of ionization. At equilibrium, the conc. of the base will be directly proportional to the conc. of the OH′-ion, and consequently also with water in excess, inversely proportional to the conc. of the H˙-ion; and if this hydrolyzed product be the compound which passes into the violet form by a slow reaction, the colour change will be proportional to the conc. of the OH′-ion, and inversely as the conc. of the H˙-ion. Hence the retarding action of H˙-ions on the colour change, and precipitation. The acidity of the $[Cr(H_2O)_6]^{\cdots}$-ion was found by J. N. Brönsted and C. V. King to be governed by the ionization: $[Cr(H_2O)_6]^{\cdots}\rightleftharpoons H^{\cdot}+[Cr(OH)(H_2O)_5]^{\cdot\cdot}$, and the variation of the ionization constant, K, with the conc. is in agreement with $\log K=\log K_a-Z_b\sqrt{\mu}$, where μ is the ionic strength; K_a, the acid ionization constant; and Z, the valency of the ion.

N. Bjerrum measured the degree of hydrolysis of soln. of chromic chloride from potential of the hydrogen electrode in the cell $H_2 \mid CrCl_{3\,soln.},KCl_{sat.\,soln.} \mid 0{\cdot}1N$-calomel electrode. Assuming that $CrCl_3+H_2O=CrCl_2(OH)+HCl$, or more simply, $Cr^{\cdots}+H_2O=Cr(OH)^{\cdot\cdot}+H^{\cdot}$, the hydrolysis constant $K=[H^{\cdot}][Cr(OH)^{\cdot\cdot}]/[Cr^{\cdots}]$. At 25° it was found that for the soln. of the dark green salt K varied from $3{\cdot}25\times10^{-6}$ to $4{\cdot}3\times10^{-6}$, and it is less marked than is the case with the soln. of the violet salt —*vide infra*. J. Olie also obtained a similar conclusion with respect to hydrolysis by showing that iodine is more rapidly separated from a mixture of potassium iodide and iodate (5 : 1) by soln. of the violet salt than is the case with soln. of the green salt. A. B. Lamb and G. R. Fonda obtained for the hydrolysis constant $K=1{\cdot}8\times10^{-6}$ to $2{\cdot}0\times10^{-6}$ calculated from the conductivities of soln. in different proportions of hydrochloric acid, and from the rate of transformation: $[Cr(H_2O)_4Cl_2]Cl\rightarrow[Cr(H_2O)_6]Cl_3$. J. Sand and F. Grammling studied the gradual hydrolysis of the green salt by sodium hydroxide. Observations were also made by H. G. Denham, and G. van Pelt.

H. de Sénarmont heated an aq. soln. of chromic chloride in a sealed tube and obtained chromic oxide. According to H. Löwel, a soln. of the green chloride in three to five times its weight of water, develops hydrogen when treated with granulated zinc in the absence of air. A blue soln. of chromous chloride is formed. If the soln. be acidified, the zinc acts more quickly. The soln. slowly deposits the chromium as oxychloride. Iron does not reduce the chromic chloride, but it forms hydrogen and chromium oxychloride. If the soln. be boiled with tin, in the absence of air, hydrogen is developed but the soln. remains green, and on cooling crystals of tin chloride are deposited.

A. del Campo obtained **chromic triaquotrichloride,** $[CrCl_3(H_2O)_3]$, by the action of hydrogen chloride on a soln. of the green chloride, $[CrCl_2(H_2O)_4]Cl.H_2O$, at 90° to 100°, under press.

A. Hiendlmayr prepared **chromic fluopentamminodichloride,** $[Cr(NH_3)_5F]Cl_2$, by the action of hydrochloric acid on a soln. of the corresponding fluoride. An aq. soln. of the yellow, four-sided plates gives no precipitate with potassium ferricyanide, but if acetone be added there is a green precipitate; hydrofluosilicic acid gives no precipitate; and sodium picrate gives a yellow precipitate consisting of fine needles.

The blue, greyish-blue, or violet hexahydrate, $CrCl_3.6H_2O$.—This salt was obtained by A. Recoura by heating a 50 per cent. soln. of the dark green chloride for some minutes at 80°, and then treating it with hydrogen chloride at 0°, when crystals of the violet hexahydrate separate out. A. Werner and A. Gubser used a similar process, boiling the soln. for an hour before treatment with hydrogen chloride at 0°. H. W. B. Roozeboom and J. Olie said that the precipitation of the violet salt by passing hydrogen chloride into soln. of the green salt previously heated to 100° is possible, because at the latter temp. the green salt rapidly passes into the violet salt with which it assumes a state of equilibrium, and the reverse change is slow enough to allow the precipitation of the violet salt at a temp. where the green salt is the stable state. A. del Campo and co-workers obtained the hexa-aquochloride by the action of hydrogen chloride on a soln. of the violet sulphate at a low temp. G. O. Higley passed hydrogen chloride into a filtered soln. of 250 grms. of chrome alum in 1000 c.c. of conc. hydrochloric acid and 250 c.c. of water at 10°–15°. The crystals were dissolved in water and again precipitated with hydrogen chloride, and freed from the green isomer by washing with acetone. N. Bjerrum used the following process :

> Hydrogen chloride was passed into a soln. of 40 grms. of enneahydrated chromic nitrate in 40 grms. of water and 40 c.c. of 38 per cent. hydrochloric acid, cooled by running water. The precipitate was washed on asbestos with fuming hydrochloric acid, mixed with 30 c.c. of conc. hydrochloric acid and again precipitated with hydrogen chloride. The mother-liquor was decanted from the crystals. The crystals were then washed with acid-free acetone, and dried over sulphuric acid in vacuo. The yield was 24·5 grms.—theoretical 26·7 grms.

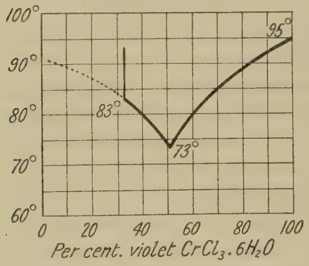


FIG. 76.—Melting-point Curve of the Dark Green and Violet $CrCl_3.6H_2O$.

Analyses in agreement with the formula $CrCl_3.6H_2O$ were made by A. Werner and A. Gubser, and R. F. Weinland and A. Koch—A. Recoura gave $CrCl_3.6\frac{1}{2}H_2O$. The colour of this form of chromic chloride ranges from grey to violet. According to J. Olie, they form six-sided, monoclinic prisms—R. F. Weinland and A. Koch added that lozenge-shaped plates are rare. W. Biltz and E. Birk gave 1·800 for the sp. gr. at 25°/4° ; and 148·1 for the mol. vol. J. Olie found the m.p. of the violet form to be 95°, and the m.p. curve of mixtures of the violet and dark green forms is shown in Fig. 76. The natural m.p.—**10**. 57, 5—of the green form is 83°, but that temp. really represents a mixture of the green form with 36 per cent. of the violet chloride. By extrapolation, the m.p. of the green chloride is over 90°. The salt can be slowly heated to 100° in vacuo without melting. Unlike the dark green salt, the violet chloride loses no water when confined over sulphuric acid at ordinary temp. S. Aoyama and co-workers studied the X-ray absorption and constitution. E. Feytis found the magnetic susceptibility to be $22·2 \times 10^{-6}$ mass unit ; and R. H. Weber made observations on this subject. A. Werner and A. Gubser found that the violet salt is more hygroscopic than the dark green salt ; it is easily soluble in water. As in the case of the dark green salt, the solubility, S per cent., of the violet chloride at 25° gradually increases with time owing to its passage into the green isomer. After a maximum of 72·22 per cent. has been attained, there follows a slow separation of the green salt (where the data are superscribed with an asterisk) :

Time .	$\frac{1}{6}$	4·5	24	48	96	120	216	288 hours.
S . .	61·99	63·19	63·88	66·16	70·68	72·22	68·95	70·01 per cent.
Violet .	98·47	96·70	91·54	83·37	69·11	62·20	54·63	46·39 ,,
Green .	1·53	3·30	8·46	16·63	30·89	37·80*	45·47*	53·61* ,,

A. Recoura gave 12·02 Cals. for the heat of soln. per mol ; and for the heat of formation $(CrCl_3.6H_2O)$=18·6 Cals. J. Olie estimated the heat of transformation from the dark green isomer to be −2·66 Cals. N. Bjerrum found that the violet salt passes into the green form particularly if moisture be present. J. Olie found the violet salt to be almost insoluble in absolute alcohol ; whereas A. Werner and A. Gubser said that it is easily soluble in alcohol, and insoluble in acetone. The behaviour of the salt on drying ; on treatment with silver nitrate ; and the conductivity of its aq. soln. are taken to be in agreement with the assumption that the violet salt is **chromic hexaquotrichloride,** $[Cr(H_2O)_6]Cl_3$, with no masked chlorine atoms. L. A. Welo gave $22·4 \times 10^{-6}$ mass units for the magnetic susceptibility.

Aq. soln. of the violet hexahydrate are violet ; and H. Löwel, and A. Recoura obtained the violet soln. by adding barium chloride to a soln. of the violet sulphate.

A. Recoura observed that if hydrated chromic oxide be precipitated from the green soln., and then dissolved in hydrochloric acid, a violet soln. is obtained. J. Olie obtained the violet soln. by adding alkali salts to the green soln., or by shaking the green soln. with barium carbonate, and dissolving the gelatinous hydrated chromic oxide in acids. J. Olie, and N. Bjerrum found that the velocity of transformation of the green into the violet soln. is favoured by a high degree of hydrolysis of the soln.; and A. B. Lamb observed that sodium acetate accelerated the transformation from green to violet soln., while A. Recoura, and L. Godefroy showed that acids retard the transformation, and N. Bjerrum found that nitrates favour the green chloride. V. V. Kuriloff observed that the transformation from green to violet soln. is favoured by exposure to light. There appears to be a state of equilibrium between the green and violet hexahydrates in aq. soln. which is slowly attained. Thus, at 25°, J. Olie found that with a green soln. of the percentage conc., *C*, the percentage proportions of the two hexahydrates in the soln. when equilibrium is attained, are

C .	3	19·70	22·72	34·70	50·19	57·57	68·50 per cent.
Violet .	100	93·1	95·1	87·1	68·7	60	42·5 ,,
Green .	0	6·9	4·9	12·9	31·3	40	57·5 ,,

The same state of equilibrium is attained if a violet soln. be used, for in that case the violet salt slowly passes into the green salt until equilibrium is attained. It will be observed that the more dilute the soln., the greater the corresponding proportion of violet salt for the equilibrium state. Raising the temp. results in an increase in the proportion of green salt. Thus, at 84°,

C . .	53·7	55·8	60·8	80·25 per cent.
Violet . .	68·10	48·51	48·15	37·35 ,,
Green . .	31·90	51·49	51·85	62·65 ,,

The speed of the transformation was measured by N. Bjerrum by measuring the change in the electrical conductivity or the change in the vol. of the soln.; and A. Heydweiller, by measuring the change in the conductivity, and in the sp. gr. of the soln. I. Koppel, and A. Werner and A. Gubser found that the velocity of transformation increases with the decreasing conc., and with increasing temp. Thus, with soln. containing a mol of chromic chloride in 125 litres of water, the molar conductivities μ mho, after the elapse of different periods of time, were

Time . .	0	2	6	10	22	32	375 mins.
μ . . .	110·9	134·8	166·1	181·3	211·9	225·4	307·4 mhos.

at 25°, and at 0°, changing the unit from minutes to hours,

Time .	0	0·5	6	18	24	73	88 hrs.
μ .	56·6	60·0	81·2	106·6	115·9	149·7	164·2 mhos.

and A. Heydweiller gave for soln. with 0·427 and 0·853 mols of the green salt per litre,

Time . .	0	7	12	20	40	61	153 min.
μ 0·427 .	42·75	57·81	62·33	65·60	67·53	67·67	— mhos.
0·853 .	—	79·85	84·3	89·0	96·0	98·0	99·7 ,,

N. Bjerrum found the results did not agree with the velocity equation for monomolecular reactions; but the results were better represented by velocity equations for two consecutive, bimolecular reactions, on the assumption that the reaction involves the sequence of changes: $[Cr(H_2O)_4Cl_2]Cl \rightarrow [Cr(H_2O)_5Cl]Cl_2 \rightarrow [Cr(H_2O)_6]Cl_3$. If *x*, *y*, *z* respectively denote the concentrations of these three salts, then $dx/dt=-k_1x$, and $dx/dt=k_2y$. It was found that at 25°, $k_1=0{\cdot}00272+0{\cdot}0000162/s$, and $k_2=(31/s+0{\cdot}005/s^2)10^{-7}$, where *s* denotes the conc. of free hydrochloric acid. For soln. with *M* mols of dark green chromic chloride, the percentage conversion, x, at the time t minutes, is as follows. With $M=0·008$ at 1° in aq. soln.,

Time . .	20	80	890	1490	4430	∞ mins.
x . .	2·5	8·3	38·8	32·9	80·1	100·0 mhos.

For $M=0·00322$ at 25° in aq. soln.,

Time . .	2	6	30	90	120	210 mins.
x . .	15·7	30·8	61·3	82·0	86·6	93·9 mhos.

For $M=0·01074$ at 25° in aq. soln.,

Time . .	3	9	30	90	180	∞ mins.
x . .	13·9	27·9	49·1	69·6	81·2	100·0 mhos.

The addition of chlorides displaces the equilibrium: $Cr(H_2O)_6^{\cdot\cdot\cdot}+3Cl' \rightleftharpoons [CrCl(H_2O)_5]^{\cdot\cdot}+2Cl'+H_2O \rightleftharpoons [CrCl_2(H_2O)_4]^{\cdot}+Cl'+2H_2O$, in accord with the law of mass action, namely, from left to right. For $M=0·01007$ at 25° in the presence of 0·0100N-NaCl,

Time . .	3	9	33	68	451	1564 mins.
x . .	13·9	27·9	51·4	65·2	94·0	99·9 mhos.

Similarly, hydrochloric acid favours the green chloride. For $M=0·00965$ at 25° in the presence of 0·01020N-HCl,

Time . .	20	60	100	290	2754	7140 mins.
x . .	3·8	11·4	18·0	38·4	76·7	94·5 mhos.

The effect of temp. is very pronounced—between 1° and 25°, k_1 increases 4·8 times per 10°, and k_2, 4 times. M. E. Baldwin also studied the effect of neutral chlorides on the transformation, and found that the hydrogen-ion conc. of chromium chloride soln. is increased by the presence of neutral chlorides, although the total amount of acid hydrogen remains constant. When the salts are arranged in order of increasing effect, the following series is obtained: (KCl, NH_4Cl), $NaCl$, $LiCl$, $BaCl_2$. I. Koppel found that in alcoholic soln., the transformation increases with dilution and with temp. With a mol of the salt in 214·36 litres of alcohol at 0°,

Time . .	12	18	24	42	95	∞ min.
x . .	5·71	7·15	8·32	10·99	14·79	16·80 mhos.

and with a mol of the salt in 273·9 litres of alcohol at 0°,

Time . .	10	30	81	141	231	∞ mins.
x . .	2·88	5·47	8·50	9·95	10·95	11·25 mhos.

N. Bjerrum found that there is a marked contraction in vol. as the green soln. passes into the violet soln.; a mol of the green salt per litre, at 25°, changes the sp. gr. of the soln. from 1·125 to 1·139 as it passes into the violet. The sp. gr. of soln. of the violet hexahydrate have not been directly determined, although some observations of A. Heydweiller gave approximate values—*vide infra*. For the effect of the violet salt on the critical soln. temp. of some binary mixtures, *vide supra*, the dark green salt. Expressing conc. by the number of grams of the salt, $CrCl_3.6H_2O$, in 100 grms. of water, G. Marchetti found for the lowering of the f.p.,

$CrCl_3.6H_2O$ . .	0·9698	2·2345	5·0046	8·1770	12·5039
F.p. . .	−0·240°	−0·0520°	−1·195°	−2·100°	−3·560°

and the calculated values for the mol. wt. range from 60·7 to 81·6. A. Werner and A. Gubser also obtained mol. wts. 74·8 to 79·1 from observations on the f.p. The theoretical value is 266·6, so that it is inferred that the ionization of the salt furnishes 4 ions. F. Jost obtained mol. wts. of 54·7 and 60·3 from the b.p. of soln. of the violet chloride in methyl alcohol. A. Recoura gave for the thermal value of the reaction $CrCl_{3\,\text{violet soln.}}+3NaOH_{\text{soln.}}=Cr(OH)_3+3NaCl+22·2$ Cals., and the precipitated hydroxide gives a blue soln. in hydrochloric acid and develops 20·7 Cals. The absorption spectrum of the soln. was discussed in connection with that of the dark green hydroxide, and there is a broad red absorption band in addition to the bluish-green band. N. Bjerrum gave for the molar electrical conductivity, μ mho, of aq. with M mols of salt per litre, at 25°,

M .	0·00097	0·00195	0·00390	0·00779	0·01559	0·03118
μ .	457·7	420·5	384·6	353·1	324·6	295·2

Measurements were also made by A. Werner and A. Gubser, A. Heydweiller, L. G. Winston and H. C. Jones, and E. J. Schaeffer and H. C. Jones. A. W. Speransky also found that the conductivity of the violet soln., at 25°, is $\mu_{25°}=324·5$ when that of the green soln. under similar conditions is $\mu_{25°}=126$. This is taken to prove that the violet salt furnishes more ions per mol than is the case with the green salt. F. Jost found for the conductivity of the violet salt in methyl alcohol,

M . . .	90·99	59·77	32·12	25·39	16·87
μ . . .	97·7	90·1	78·7	74·1	67·7 mhos.

K. Hopfgartner found the transport numbers for violet chromic chloride in 1·00, 0·32, and 0·075 eq. soln. to be respectively 0·318, 0·357, and 0·414, or extrapolating to zero concentration, 0·446. The mobilities of the ions are respectively 53, 49·5, and 46·3. These results indicate that the chromic ion is probably surrounded by a fairly large water sheath. N. Bjerrum found the constant of hydrolysis, as in the case of the dark green salt, and the percentage degree of hydrolysis, to be :

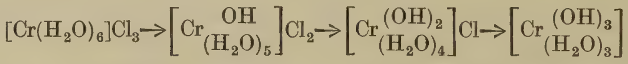
		0°	25°	50°	75°	100°
K . . .		0·000022	0·000098	0·00034	0·00103	0·00264
Hydrolysis	0·1M-	1·5	3·1	5·7	9·6	15·0 per cent.
	0·001M-	13·8	26·7	43·7	62·3	77·4 ,,

A. B. Lamb and G. R. Fonda gave $K=1·58\times10^{-4}$ at 25°. N. Bjerrum's value was $K=0·98\times10^{-4}$ at 25°. H. G. Denham, and G. van Pelt made observations on this subject, for the violet hexahydrate is intermediate between the value for aluminium chloride $K=0·14\times10^{-4}$, and the value for ferric chloride, 25×10^{-4}. Observations were made by J. N. Brönsted and K. Volqvartz. K. H. Gustavson found that the addition of progressive amounts of sodium chloride to soln. of chromic chloride causes an initial increase in the H˙-ion conc. represented by the value of p_H, and this is followed by a decrease with greater conc. of the sodium chloride. The latter effect is due to the increase in conc. of the chromium salt by hydration of the sodium chloride. The former change is most marked in dil. soln. of lesser acidity. It is supposed to be due to changes in the composition of the internal sphere in the chrome complex, different modifications of the basic aquo-chromic chlorides existing analogous to the normal chlorides $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2$, and $[Cr(H_2O)_4Cl_2]Cl$. The addition of sodium chloride will favour the formation of compounds with chlorine co-ordinately attached, and the increase in chlorine ions is evidenced by decrease in the electric charges of the cation and by an increase, in p_H. If sodium chloride is replaced by magnesium chloride, this effect is masked by the greater hydration tendency of the magnesium salt. The point at which precipitation occurs during addition of sodium hydroxide is not a function of p_H, but is proportional to the ratio of chlorine to chromium in the complex cation.

J. Sand and F. Grammling measured the velocity with which the violet hexahydrate liberates iodine from a mixture of potassium iodide and iodate, and found the results to be in agreement with the assumption that the molecule is $Cr_2Cl_6.12H_2O$, and not $[Cr(H_2O)_6]Cl_3$. H. W. Fischer found that the solubility of chromium hydroxide in an aq. soln. of green chromic chloride is not directly proportional to the conc. of the latter. A basic chloride is probably formed. From a soln. of chromium hydroxide in aq. chromic chloride, the former cannot be precipitated either by the addition of electrolytes or by the action of heat ; part of it is supposed to be in soln. in the colloidal form and part in the form of a compound containing chlorine. C. R. C. Tichborne said that, owing to hydrolysis, the green colour of the chromic salts is due to the formation of basic salts. The fact that the simplest way to convert the green soln. into a violet soln. is by boiling; that the change in colour of the green soln. is accompanied by the liberation of an acid, and the fact that incomplete precipitations with silver nitrate (and barium chloride) is a property common with elements known to be colloidal, led H. T. S. Britton to assume that the green soln. contain colloidal chromium hydroxide in which the cations of the colloidal electrolyte consist of chromium hydroxide associated with varying amounts of acid radicle. He showed that at 18°, 0·0133N-soln. of blue and green chromic chloride have respectively an e.m.f. of 0·467 and 0·409 volt against the N-calomel electrode; the $H^{\cdot}$-ion conc. are $p_H=3·19$ and 2·18; and the percentage hydrolysis 1·62 and 16·4. In the electrometric titration with sodium hydroxide, precipitation began when the e.m.f. were respectively 0·588 and 0·586 volt, when $p_H=5·28$ and 5·25; or when 1·07 and 1·43 eq. of NaOH per eq. of Cr had been added; and precipitation was complete when 2·78 and 2·15 eq. of alkali had been added. J. E. Howard and W. H. Patterson found that the effect of the violet and green salts on the critical soln. temp. of various mixtures is much greater than would be the case if the difference in the green and violet salts were due to the presence of basic, colloidal aggregates in the former. Colloids, *per se*, have usually a very small influence on the critical soln. temp. A. W. Ralston and J. A. Wilkinson found that soln. of the green and violet salts in liquid hydrogen sulphide are non-conducting.

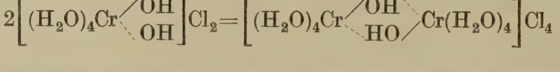
A. Recoura passed hydrogen chloride into a soln. of chromic chloride for some days. The soln. turns brown and then red, presumably because of the formation of a soluble complex $CrCl_3.nHCl$. On adding ether, this complex is precipitated in unstable green needles. R. Schwarz and G. Meyer found that while anhydrous chromic chloride does not take up hydrogen chloride readily, the violet hexahydrated chloride forms some complexes; and the green salt $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ forms some complex chlorochromic acids at −50°, namely **tetrachlorochromic acid,** $CrCl_3.HCl.6·5H_2O$, **pentachlorochromic acid,** $CrCl_3.2HCl.8·5H_2O$, and **hexachlorochromic acid,** $CrCl_3.3HCl.10·5H_2O$, as dark green compounds which decompose when heated. J. R. Partington and S. K. Tweedy obtained impure tetrachlorochromic acid, $CrCl_3.HCl.6H_2O$, as a precipitate by slowly saturating at 0° a conc. soln. of dark green chromic chloride mixed with an equal vol. of ether. It is washed with dry ether.

The hydrolysis of chromic chloride formerly represented by $CrCl_3+H_2O \rightleftharpoons Cr(OH)Cl_2+HCl$; $Cr(OH)Cl_2+H_2O \rightleftharpoons Cr(OH)_2Cl+HCl$; and $Cr(OH)_2Cl+H_2O \rightleftharpoons Cr(OH)_3+HCl$, is now represented by A. Werner, and P. Pfeiffer as involving the formation of hydroxyl-compounds in the stages:



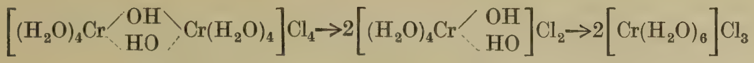
$$[Cr(H_2O)_6]Cl_3 \rightarrow \left[Cr\begin{matrix}OH\\(H_2O)_5\end{matrix}\right]Cl_2 \rightarrow \left[Cr\begin{matrix}(OH)_2\\(H_2O)_4\end{matrix}\right]Cl \rightarrow \left[Cr\begin{matrix}(OH)_3\\(H_2O)_3\end{matrix}\right]$$

With increasing hydrolysis, the $H^{\cdot}$-ion conc. of the soln. also increases. According to N. Bjerrum, with ageing, or more rapidly with heating, the hydroxyl compounds suffer an internal change producing the so-called *ol-salts*, which in contact with acids, are more stable than the hydroxyl salts. The action is represented graphically:



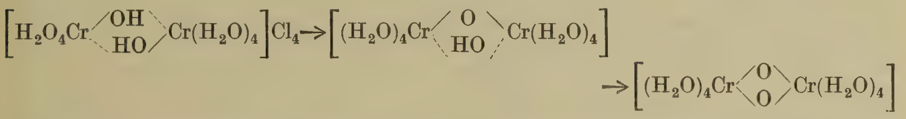
$$2\left[(H_2O)_4Cr\begin{matrix}OH\\OH\end{matrix}\right]Cl_2=\left[(H_2O)_4Cr\begin{matrix}OH\\HO\end{matrix}Cr(H_2O)_4\right]Cl_4$$

so that the molecular vol. of the salt in soln. increases and may assume the character of the colloid. When an acid is added to a hydroxyl compound some is consumed in reversing the change to form an aquo-compound $[Cr-OH]+HCl=[Cr...H_2O]Cl$, but with an ol-salt the first addition of acid simply increases the acidity of the soln., and thereafter gradually reforms the hydroxyl salt which then passes into the aquo-salt:



$$\left[(H_2O)_4Cr\left\langle\begin{matrix}OH\\HO\end{matrix}\right\rangle Cr(H_2O)_4\right]Cl_4\rightarrow 2\left[(H_2O)_4Cr\left\langle\begin{matrix}OH\\HO\end{matrix}\right.\right]Cl_2\rightarrow 2\left[Cr(H_2O)_6\right]Cl_3$$

The resistance offered by the different chromium complex salts to this change depends on the nature of the complex radicles—chloride, sulphate, formate, oxalate, etc. With longer ageing, or heating, a more drastic, irreversible, internal change occurs, which, according to D. Balanyi, results in the formation of oxy-salts, a change which makes the mother-liquor more acidic, thus:



$$\left[H_2O_4Cr\left\langle\begin{matrix}OH\\HO\end{matrix}\right\rangle Cr(H_2O)_4\right]Cl_4\rightarrow\left[(H_2O)_4Cr\left\langle\begin{matrix}O\\HO\end{matrix}\right\rangle Cr(H_2O)_4\right]\rightarrow\left[(H_2O)_4Cr\left\langle\begin{matrix}O\\O\end{matrix}\right\rangle Cr(H_2O)_4\right]$$

The resulting product is not attacked by standing in contact with cold dil. hydrochloric acid.

E. Stiasny and O. Grimm found that the properties of chromic chloride soln. depend largely on whether the liquor is heated before being rendered basic, on the degree of basicity, on the heating or ageing after being rendered basic, and on ageing after heating. When a basic chromium chloride soln. is boiled for 5 mins. the p_H value alters and only recovers after three days. It also decreases on ageing until it reaches 2·79 after four weeks; the addition of hydrochloric acid postpones the "ageing" effect. Heating before rendering the soln. basic causes chlorine to enter the chromium complex, but there is no chlorine in the complex after the soln. has been rendered basic and aged for a short time. The boiling of the soln. before rendering it basic encourages the formation of "ol" compounds; "ageing" has the same effect. Boiling is more effective in the formation of "ol" compounds and oxygen bridges after the liquor has been made basic than before. Heating increases the precipitation value both of normal and basic chromic chloride soln. owing to the formation of "ol" compounds which are less easily precipitable than the hydroxy-compounds. The heating effect is more pronounced with the more basic salts. Ageing diminishes the precipitation value of heated soln. of normal chloride which have not been heated, and of soln. of the basic salt which have been heated before and after rendering basic, but increases the value for basic soln. which have been boiled before rendering basic only. The dialytic properties of the different types of chromium chloride soln. are almost the same, showing that conversion into "ol" compounds does not result in the formation of large molecules unless the basicity exceeds 33 per cent. T. Murayasu found that the electrical conductivity of the soln. of chromic chloride is increased by adding glycocoll.

REFERENCES.

[1] A. Moberg, *Dissertatio de chloreto chromoso*, Helsingfors, 1843; *Journ. prakt. Chem.*, (1), **29**. 175, 1843; (1), **44**. 322, 1848; F. Hein, J. Reschke and F. Pintus, *Ber.*, **60**. B, 749, 1927; E. M. Péligot, *Compt. Rend.*, **19**. 609, 734, 1844; *Ann. Chim. Phys.*, (3), **12**. 528, 1844; H. Moissan, *ib.*, (5), **25**. 403, 1882; *Compt. Rend.*, **92**. 792, 1881; G. Chesneau, *ib.*, **129**. 100, 1899; A. Mailfert, *ib.*, **94**. 797, 860, 1186, 1882; A. Recoura, *ib.*, **100**. 1227, 1885; **101**. 435, 1885; **102**. 865, 1886; *Recherches sur les chlorûres de chrome*, Paris, 1886; *Ann. Chim. Phys.*, (6), **10**. 10, 1887; H. Löwel, *ib.*, (3), **40**. 45, 1854; G. Baugé, *ib.*, (7), **19**. 158, 1900; *Bull. Soc. Chim.*, (3), **19**. 552, 1896; *Compt. Rend.*, **122**. 474, 1899; **125**. 1177, 1897; **126**. 1566, 1898; M. Berthelot, *ib.*, **127**. 24, 1898; *Ann. Chim. Phys.*, (7), **15**. 289, 1898; J. W. McBain, *Zur Kenntnis der Katalyse in heterogenen Systemen—die Zersetzung des Chromochlorüre mit kolloiden Platin*, Heidelberg, 1909; M. Prud'homme, *Bull. Soc. Mulhouse*, **59**. 603, 1889; J. J. Berzelius, *Oefvers. Akad. Förh.*, 207, 1844; F. Wöhler, *Pogg. Ann.*, **11**. 148, 1827; W. Hampe, *Chem. Ztg.*, **12**. 4, 1888; T. Döring, *Journ. prakt. Chem.*, (2), **66**. 65, 1902; L. F. Nilson and O. Pettersson, *Compt. Rend.*, **107**. 529, 1888; *Zeit. phys. Chem.*, **2**. 673, 1888; *Journ. Chem. Soc.*, **53**. 828, 1888; G. Herrmann, *Ueber die elektrolytische Darstellung von Chromosalzen*, München, 51, 1909; A. Asmanoff, *Zeit. anorg. Chem.*, **160**. 209, 1927; F. W. Clarke and J. P. Grabfield, *Amer. Chem.*

Journ., **5.** 240, 1884 ; R. Stahn, *Ein Beitrag zur Chemie des zweiwertigen Chroms*, Berlin, 1926 ; I. Koppel, *Zeit. anorg. Chem.*, **45.** 361, 1905 ; P. Rohland, *ib.*, **21.** 38, 1899 ; F. O. von der Pfordten, *Liebig's Ann.*, **228.** 112, 1885 ; C. E. Ufer, *ib.*, **112.** 302, 1859 ; W. A. Knight and E. M. Rich, *Journ. Chem. Soc.*, **99.** 89, 1911 ; E. S. Hedges and J. E. Myers, *ib.*, **125.** 604, 1928 ; K. Jablczynsky, *Anz. Akad. Krakau*, 398, 1908 ; *Abh. Akad. Krakau*, **48.** 75, 1908 ; *Zur Kenntnis der Katalyse in heterogenen Systemen*, Freiburg, 1908 ; *Zeit. phys. Chem.*, **64.** 748, 1908 ; G. S. Forbes and H. W. Richter, *Journ. Amer. Chem. Soc.*, **39.** 1140, 1917 ; N. H. Furman, *ib.*, **50.** 755, 1675, 1928 ; M. C. Taylor, W. A. Gersdorff and E. J. Tovrea, *ib.*, **44.** 612, 1922 ; M. C. Taylor, *U.S. Pat. No.* 1369204, 1921 ; K. Jellinek and R. Koop, *Zeit. phys. Chem.*, **145.** 305, 1929 ; R. Koop, *Ueber heterogene Gleichgewichte von Metallhalogeniden mit Wasserstoff bzw. Chlorwasserstoff*, Danzig, 1929 ; W. Manchot and J. Herzog, *Ber.*, **33.** 1742, 1900 ; **59.** B, 1171, 1180, 1926 ; W. Peters, *ib.*, **42.** 4826, 1909 ; *Zeit. anorg. Chem.*, **77.** 137, 1912 ; W. Traube and W. Lange, *Ber.*, **58.** B. 2773, 1925 ; **59.** B, 2860, 1926 ; W. Traube and A. Goodson, *ib.*, **49.** 1679, 1916 ; W. Traube and W. Passarge, *ib.*, **46.** 1505, 1913 ; **49.** 1692, 1916 ; W. Traube, E. Burmeister and R. Stahn, *Zeit. anorg. Chem.*, **147.** 50, 1925 ; K. Someya, *ib.*, **160.** 355, 1927 ; F. Ephraim, *Ber.*, **50.** 1067, 1917 ; F. Ephraim and S. Millmann, *ib.*, **50.** 529, 1917 ; R. H. Weber, *Ann. Physik*, (4), **36.** 624, 1912 ; S. Meyer, *ib.*, (4), **1.** 664, 1900 ; *Wied. Ann.*, **68.** 325, 1899 ; **69.** 236, 1899 ; B. Cabrera and S. P. de Rubies, *Anal. Fis. Quim.*, **17.** 149, 1919 ; G. Breitand H. K. Onnes, *Proc. Akad. Amsterdam*, **26.** 840, 1923 ; W. Biltz and E. Birk, *Zeit. anorg. Chem.*, **134.** 125, 1924 ; **150.** 20, 1925 ; E. Zinth and G. Rienäcker, *ib.*, **161.** 374, 385, 1927 ; H. Brintzinger and F. Rodis, *Zeit. Elektrochem.*, **34.** 246, 1928 ; H. Brintzinger and F. Oschatz, *Zeit. anorg. Chem.*, **165.** 221, 1927 ; K. Someya, *ib.*, **161.** 46, 1927 ; *Science Rep. Tohoku Univ.*, **16.** 411, 1927 ; V. Rothmund, *Zeit. anorg. Chem.*, **62.** 108, 1909 ; K. Kraut, *Chem. Ztg.*, **10.** 820, 1886 ; R. Ripan, *Bull. Soc. Stiinte*, **4.** 28, 1928 ; R. P. Anderson and J. Riffe, *Journ. Ind. Eng. Chem.*, **8.** 24, 1916 ; H. Küssner, *Zeit. Elektrochem.*, **16.** 754, 1910 ; *Ueber das anodische Verhalten des Molybdäns, Mangans, Chroms und Tantals*, Halle a. S., 1910 ; W. Gregory, *Journ. prakt. Chem.*, (1), **3.** 52, 1834 ; *Journ. Pharm. Chim.*, (2), **20.** 413, 1834 ; F. Allison and E. J. Murphy, *Journ. Amer. Chem. Soc.*, **52.** 3796, 1930 ; H. Wieland and F. G. Fischer, *Ber.*, **59.** B, 1171, 1926 ; J. S. and O. Burger, *ib.*, **39.** 1771, 1906 ; V. Kohlschütter, *ib.*, **37.** 3053, 1904 ; **40.** 877, 1907 ; F. Hein, I. Reschk and F. Pintus, *ib.*, **60.** B, 749, 1927 ; F. Pintus, *Ueber die Existenz des einwertigen Chroms und den Einfluss der Komplexkonstitution auf die Bildung chromorganischer Verbindungen*, Leipzig, 1928.

[2] F. Hein, J. Reschke and F. Pintus, *Ber.*, **60.** B, 679, 1927 ; A. Moberg, *Dissertatio de chloreto chromoso*, Helsingfors, 1843 ; *Journ. prakt. Chem.*, (1), **29.** 175, 1843 ; (1), **44.** 322, 1848 ; L. F. Nilson and O. Pettersson, *Compt. Rned.*, **107.** 529, 1888 ; *Zeit. phys. Chem.*, **2.** 673, 1888 ; *Journ. Chem. Soc.*, **53.** 828, 1888 ; J. von Liebig, *Pogg. Ann.*, **21.** 359, 1831 ; J. J. Berzelius, *Schweigger's Journ.*, **22.** 53, 1818 ; *Pogg. Ann.*, **1.** 34, 1824 ; **50.** 79, 1840 ; L. N. Vauquelin, *Ann. Chim. Phys.*, (1), **25.** 21, 194, 1798 ; (1), **70.** 70, 1809 ; J. H. Kastle, *Amer. Chem. Journ.*, **23.** 500, 1900 ; S. Meyer, *Ann. Physik*, (4), **1.** 664, 1900 ; *Wied. Ann.*, **68.** 325, 1899 ; **69.** 236, 1899 ; G. Quincke, *ib.*, **24.** 347, 1885 ; **34.** 401, 1888 ; G. Jäger and S. Meyer, *ib.*, **67.** 427, 707 ; 1899 ; *Sitzber. Akad. Wien*, **106.** 594, 623, 1897 ; **107.** 5, 1898 ; W. Eidmann, *Ein Beitrag zur Erkenntnis des Verhaltnis chemischer Verbindungen in nichtwässrigen Lösungen*, Giessen, 1899 ; H. Arctowsky, *Zeit. anorg. Chem.*, **6.** 257, 1894 ; P. A. Thiessen and B. Kandelaky, *ib.*, **181.** 285, 1929 ; P. Rohland, *ib.*, **21.** 39, 1899 ; I. Koppel, *ib.*, **28.** 471, 1901 ; P. Pfeiffer, *ib.*, **36.** 349, 1903 ; **55.** 97, 1907 ; R. F. Weinland and C. Feige, *Ber.*, **36.** 244, 1903 ; A. Naumann, *ib.*, **42.** 3790, 1909 ; **47.** 1369, 1914 ; F. Hein, *ib.*, **52.** B, 195, 1919 ; F. Ephraim, *ib.*, **50.** 1069, 1917 ; O. Stelling, *ib.*, **60.** B, 650, 1927 ; *Zeit. Elektrochem.*, **34.** 520, 1928 ; **36.** 605, 1930 ; *Zeit. Physik*, **50.** 506, 1928 ; *Zeit. phys. Chem.*, **7.** B, 325, 1930 ; *Ber. Skand. Naturforskermöde*, **18.** 503, 1929 ; K. Jellinek and R. Koop, *Zeit. phys. Chem.*, **145.** 305, 1929 ; R. Koop, *Ueber heterogene Gleichgewichte von Metallhalogeniden mit Wasserstoff bzw. Chlorwasserstoff*, Danzig, 1929 ; N. Bunge, *Chem. Centr.*, (2), **10.** 257, 1865 ; J. Y. Johnson, *Brit. Pat. Nos.* 269028, 271016, 1926 ; F. M. Jackson, *ib.*, 276120, 1926 ; A. W. Cronander, *Oefvers. Akad. Stockholm*, **27.** 57, 1870 ; *Ber.*, **6.** 1466, 1873 ; *Bull. Soc. Chim.*, (2), **19.** 499, 1873 ; G. M. Bennett and E. E. Turner, *Journ. Chem. Soc.*, **105.** 1057, 1914 ; W. R. Lang and C. M. Carson, *Journ. Amer. Chem. Soc.*, **26.** 758, 1904 ; *Proc. Chem. Soc.*, **19.** 147, 1903 ; W. R. Lang and E. H. Jolliffe, *ib.*, **19.** 147, 1903 ; M. Crespi, *Anal. Fis. Quim.*, **26.** 152, 1928 ; H. R. Woltjer, *Comm. Phys. Lab. Leiden*, 173, b, 1925 ; *Proc. Akad. Amsterdam*, **28.** 536, 1925 ; *Versl. Akad. Amsterdam*, **34.** 491, 1925 ; H. R. Woltjer and H. K. Onnes, *ib.*, **34.** 502, 1925 ; *Comm. Phys. Lab. Leiden*, 173, c, 1925 ; W. Biltz and E. Birk, *Zeit. anorg. Chem.*, **134.** 125, 1924 ; K. Someya, *ib.*, **160.** 355, 1927 ; **169.** 293, 1928 ; R. Schenck and G. Meyer, *ib.*, **166.** 113, 1927 ; R. Schwarz and G. Meyer, *ib.*, **166.** 190, 1927 ; A. E. Lindh, *Zeit. physik*, **6.** 303, 1921 ; L. A. Welo, *Phil. Mag.*, (7), **6.** 481, 1928 ; G. Natta, *Atti Accad. Lincei*, (6), **5.** 592, 1927 ; H. F. Gaultier de Claubry, *Ann. Chim. Phys.*, (2), **45.** 110, 1830 ; J. L. Lassaigne, *Phil. Mag.*, **56.** 433, 1820 ; *Ann. Chim. Phys.*, (2), **14.** 299, 1820 ; H. Moissan, *ib.*, (5), **21.** 246, 1880 ; (5), **25.** 406, 1882 ; *Compt. Rend.*, **90.** 1359, 1880 ; **92.** 1051, 1881 ; F. Bourion, *Ann. Chim. Phys.*, (8), **21.** 56, 1910 ; C. Matignon and F. Bourion, *Compt. Rend.*, **138.** 760, 1904 ; E. Demarçay, *ib.*, **104.** 112, 1887 ; H. Quantin, *ib.*, **99.** 707, 1884 ; **104.** 223, 1887 ; E. Feytis, *ib.*, **156.** 886, 1913 ; V. A. Jacquelin, *ib.*, **24.** 679, 1847 ; P. Camboulives, *ib.*, **150.** 175, 1910 ; T. Peczalsky, *ib.*, **182.** 516, 1926 ; A. Recoura, *ib.*, **100.** 1227, 1885 ; **102.** 922, 1886 ; *Recherches sur les chlorures de chrome*, Paris, 1886 ; *Ann. Chim. Phys.*, (6), **10.** 49, 1887 ; J. Pelouze, *ib.*, (3), **14.** 251, 1845 ; J. Persoz, *ib.*, (2), **44.** 315, 1830 ; A. Michaelis, *Jena Zeit.*, **6.** 239, 1871 ; *Journ. prakt. Chem.*, (2), **4.** 449, 1871 ; *Bull. Soc. Chim.*, (2), **17.** 205, 1872 ; L. Hackspill, *Bull.*

Soc. Chim., (4), **1**. 896, 1907 ; L. R. von Fellenberg, *Pogg. Ann.*, **50**. 61, 1840 ; F. Pintus, *Ueber die Existenz des einwertigen Chroms und den Einfluss der Komplexkonstitution auf die Bildung chromorganischer Verbindungen*, Leipzig, 1928 ; T. Peczalsky and J. Cichocky, *Compt. Rend.*, **188**. 699, 1929 ; F. Wöhler, *Liebig's Ann.*, **111**. 233, 1859 ; *Pogg. Ann.*, **11**. 148, 1827 ; H. Rose, *ib.*, **24**. 333, 1832 ; **42**. 541, 1837 ; **45**. 183, 1838 ; C. Brunner, *Mitt. Naturforsch-Ges. Bern*, 163, 1860 ; *Dingler's Journ.*, **159**. 356, 1861 ; A. Schötter, *Liebig's Ann.*, **37**. 148, 1841 ; C. E. Ufer, *ib.*, **112**. 284, 1859 ; G. Rauter, *ib.*, **270**. 251, 1892 ; A. Geuther, *ib.*, **118**. 61, 1861 ; M. Traube, *ib.*, **66**. 87, 165, 1848 ; A. Schafarik, *Sitzber. Akad. Wien*, **47**. 256, 1863 ; *Journ. prakt. Chem.*, (1), **90**. 12, 1863 ; A. Scott, *Proc. Roy. Soc. Edin.*, **14**. 410, 1888 ; K. Drucker, *Zeit. phys. Chem.*, **36**. 173, 1901 ; H. Kunheim, *Ueber die Einwirkung des Wasserdampfes auf Chlormetalle bei hoher Temperatur*, Göttingen, 1861 ; J. R. Mourelo, *Anal. Fis. Quim.*, **8**. 196, 1910 ; A. Vosmär, *Zeit. anal. Chem.*, **28**. 324, 1889 ; F. W. Clarke, *Amer. Journ. Science*, (3), **14**. 281, 1877 ; F. W. Clarke and J. P. Grabfield, *Amer. Chem. Journ.*, **5**. 240, 1884 ; R. D. Hall, *Journ. Amer. Chem. Soc.*, **26**. 1244, 1904 ; F. P. Venable and D. H. Jackson, *ib.*, **42**. 2531, 1920 ; *Journ. Elisha Mitchell Soc.*, **35**. 87, 1920 ; P. Curie, *Chem. News*, **28**. 307, 1873 ; H. Löwel, *Journ. Pharm. Chim.*, (3), **4**. 422, 1843 ; L. C. A. Barreswill, *ib.*, (3), **4**. 431, 1843 ; M. Bauck, *ib.*, (3), **36**. 395, 1859 ; H. Kopp, *Liebig's Ann. Suppl.*, **3**. 293, 1865 ; F. Serena, *Monit. Scient.*, (2), **7**. 708, 1870 ; W. Hampe, *Chem. Ztg.*, **12**. 4, 1888 ; P. Fireman and E. G. Porter, *Journ. Phys. Chem.*, **8**. 503, 1904 ; R. H. Weber, *Ann. Physik*, (4), **36**. 624, 1912 ; E. M. Péligot, *Compt. Rend.*, **19**. 609, 734, 1844 ; *Ann. Chim. Phys.*, (3), **12**. 528, 1844 ; C. P. Snow and F. I. G. Rawlins, *Nature*, **125**. 349, 1930 ; L. Meunier and M. Lesbre, *Compt. Rend.*, **190**. 183, 1930 ; V. N. Ipatieff and B. A. Mouromtseff, *ib.*, **183**. 505, 1926 ; *Bull. Soc. Chim.*, (4), **39**. 1384, 1926 ; G. Faseya and K. Murata, *Journ. Phys. Chem.*, **34**. 2001, 1930 ; G. Boulanger, *Compt. Rend.*, **191**. 56, 1930 ; A. Byk and H. Jaffe, *Zeit. phys. Chem.*, **681**. 323, 1910 ; H. Farl, *Ueber die Einwirkung der Chromhaloide auf Aethyläther und über Komplexverbindungen des hierbei entstehenden Chromdihalogenäthylates*, Leipzig, 1929 ; P. Krishnamurti, *Indian Journ. Phys.*, **5**. 113, 1930 ; R. F. Weinland and H. Schmid, *Zeit. anorg. Chem.*, **44**. 37, 1905 ; N. Wooster, *Zeit. Kryst.*, **74**. 363, 1930 ; N. Bunge, *Chem. Centr.*, (2), **10**. 257, 1865 ; A. Commaille, *Compt. Rend.*, **63**. 556, 1886 ; *Chem. News*, **14**. 188, 1866 ; Z. Roussin, *ib.*, **14**. 27, 1866 ; *Journ. Pharm. Chim.*, (4), **3**. 413, 1866 ; *Bull. Soc. Chim.*, (2), **6**. 23, 1866 ; C. W. Vincent, *Phil. Mag.*, (4), **24**. 328, 1862 ; T. Ishiwara, *Science Rep. Tohoku Univ.*, **3**. 303, 1914.

[3] G. N. Wyrouboff, *Bull. Soc. Chim.*, (3), **27**. 666, 1902 ; L. Godefroy, *ib.*, (2), **43**. 229, 1885 ; *Compt. Rend.*, **300**. 105, 1885 ; H. de Sénarmont, *ib.*, **32**. 762, 1851 ; E. Feytis, *ib.*, **156**. 886, 1913 ; A. Étard, *ib.*, **120**. 1057, 1895 ; A. Recoura, *ib.*, **100**. 1227, 1886 ; **102**. 515, 922, 1886 ; *Recherches sur les chlorures de chrome*, Paris, 1886 ; *Ann. Chim. Phys.*, (6), **10**. 22, 1887 ; E. M. Péligot, *ib.*, (3), **12**. 537, 1844 ; (3), **14**. 240, 1845 ; H. Löwel, *ib.*, (3), **14**. 246, 1845 ; (3), **40**. 43, 1854 ; H. Lessheim, J. Meyer and R. Samuel, *Zeit. Physik*, **43**. 299, 1927 ; A. Moberg, *Dissertatio de chloreto chromoso*, Helsingfors, 1843 ; *Journ. prakt. Chem.*, (1), **29**. 175, 1843 ; (1), **44**. 322, 1848 ; H. Rose, *Pogg. Ann.*, **45**. 183, 1838 ; J. J. Berzelius, *ib.*, **50**. 79, 1840 ; J. R. Partington and S. K. Tweedy, *Journ. Chem. Soc.*, 2899, 1927 ; *Nature*, **117**. 415, 1926 ; N. Bjerrum, *Ber.*, **39**. 1599, 1906 ; **40**. 2915, 1907 ; *Zeit. phys. Chem.*, **59**. 336, 581, 1907 ; **73**. 724, 1910 ; *Danske Vid. Selsk. Skr.*, (7), **4**. 79, 1907 ; *Zeit. anorg. Chem.*, **63**. 140, 1909 ; **119**. 165, 1921 ; *Studier over basiske Kromiforbindelser*, Kopenhagen, 1908 ; N. Bjerrum and G. H. Hansen, *ib.*, **63**. 151, 1909 ; N. Bjerrum and C. Faurholt, *Zeit. phys. Chem.*, **130**. 585, 1927 ; E. Moles and M. Crespi, *ib.*, **130**. 337, 1927 ; A. Gubser, *Ueber die Hydrate des Chromchlorids*, Zürich, 1900 ; A. Werner and A. Gubser, *Ber.*, **34**. 1592, 1901 ; A. Werner and R. Huber, *ib.*, **39**. 329, 1906 ; F. Jost, *ib.*, **39**. 4327, 1906 ; P. Pfeiffer, *ib.*, **34**. 2561, 1901 ; A. Hiendlmayr, *Beiträge zur Chemie der Chrom- und Kobalt-Ammoniake*, Freising, 24, 1907 ; O. Stelling, *Zeit. Elektrochem.*, **34**. 520, 1928 ; G. O. Higley, *Journ. Amer. Chem. Soc.*, **26**. 625, 1904 ; A. B. Lamb, *ib.*, **28**. 1710, 1906 ; A. B. Lamb and G. R. Fonda, *ib.*, **43**. 1154, 1921 ; A. W. Ralston and J. A. Wilkinson, *ib.*, **50**. 258, 1928 ; H. W. B. Roozeboom and J. Olie, *Proc. Akad. Amsterdam*, **8**. 66, 1905 ; J. Olie, *Zeit. anorg. Chem.*, **51**. 50, 1906 ; **52**. 62, 1907 ; **53**. 273, 1907 ; I. Koppel, *ib.*, **28**. 461, 1901 ; W. Biltz and E. Birk, *ib.*, **134**. 125, 1924 ; **150**. 20, 1925 ; R. Schwarz and G. Meyer, *ib.*, **166**. 190, 1927 ; R. F. Weinland and A. Koch, *ib.*, **39**. 328, 1904 ; R. F. Weinland and T. Schumann, *Ber.*, **40**. 3093, 1907 ; *Zeit. anorg. Chem.*, **58**. 176, 1908 ; H. W. Fischer, *ib.*, **40**. 44, 1904 ; *Untersuchungen über Metallhydroxyde*, Breslau, 1908 ; H. Jaffe, *Ueber die Absorptionsverhältnisse einiger Chrom- und Eisensalzlösungen im kurzwelligen Spektralgebiete*, Potsdam, 1909 ; A. Byk and H. Jaffe, *Zeit. phys. Chem.*, **68**. 323, 1909 ; E. Petersen, *ib.*, **4**. 384, 1889 ; J. N. Brönsted and C. V. King, *ib.*, 130, 584, 699, 1927 ; H. C. Jones, *Hydrates in Aqueous Solution*, Washington, 89, 1907 ; H. C. Jones and H. P. Bassett, *Amer. Chem. Journ.*, **34**. 309, 1905 ; E. J. Schaeffer and H. C. Jones, *ib.*, **49**. 207, 1913 ; L. G. Winston and H. C. Jones, *ib.*, **46**. 368, 1911 ; H. C. Jones and C. A. Jacobsen, *ib.*, **40**. 355, 1908 ; H. C. Jones and W. W. Strong, *Phys. Zeit.*, **10**. 499, 1909 ; H. C. Jones and J. A. Anderson, *Amer. Chem. Journ.*, **41**. 163, 1909 ; *The Absorption Spectra of Solutions*, Washington, 1909 ; H. G. Denham, *Journ. Chem. Soc.*, **93**. 51, 1908 ; H. T. S. Britton, *ib.*, **127**. 2110, 1925 ; J. E. Howard and W. H. Patterson, *ib.*, **129**. 2791, 1926 ; A. W. Speransky, *Journ. Russ. Phys. Chem. Soc.*, **25**. 1, 1893 ; V. V. Kuriloff, *ib.*, **47**. 469, 1915 ; *Koll. Zeit.*, **14**. 171, 1914 ; A. del Campo, F. Manzano and A. Mallo, *Anal. Fis. Quim.*, **25**. 186, 1927 ; G. Marchetti, *Atti Accad. Lincei*, (5), **1**. 1, 1892 ; *Gazz. Chim. Ital.*, **22**. ii, 375, 1893 ; G. Magnanini, *ib.*, **25**. 378, 1895 ; A. Piccini, *ib.*, **24**. ii, 545, 1894 ; *Zeit. anorg. Chem.*, **8**. 115, 1895 ; P. Rohland, *ib.*, **21**. 42, 1899 ; A. Heydweiller, *ib.*, **91**. 66, 1915 ; E. Stiasny and O. Grimm,

Collegium, 505, 1927; D. Balanyi, *ib.*, 86, 1927; 72, 1928; O. Grimm, *Eigenschaften und Verhalten verschieden vorbehendelter Chromchlorid- und Chromsulfat-Lösungen*, Darmstadt, 1928; N. Demassieux and J. Heyrovsky, *Journ. Chim. Phys.*, **26**. 219, 1929; A. Johnsen, *Neues Jahrb. Min.*, ii, 114, 1903; J. Sand and F. Grammling, *Zeit. phys. Chem.*, **62**. 1, 28, 1908; F. Grammling, *Studien über komplexe Chromverbindungen*, Berlin, 1909; T. Murayasu, *Hokkaido Journ. Med.*, **6**. 328, 1928; I. Koppel in R. Abegg, *Handbuch der anorganischen Chemie*, Leipzig, **4**. i, (2), 89, 1921; M. E. Baldwin, *Journ. Amer. Leather Chem. Assoc.*, **14**. 10, 1919; K. Hopfgartner, *Monatsh.*, **40**. 259, 1919; J. N. Brönsted and K. Volqvartz, *Zeit. phys. Chem.*, **134**. 97, 1928; R. H. Weber, *Ann. Physik*, (4), **36**. 624, 1912; H. de Bois and G. J. Elias, *ib.*, (4), **27**. 233, 1909; *Proc. Akad. Amsterdam*, **10**. 578, 839, 1908; G. Quincke, *Wied. Ann.*, **24**. 395, 1885; O. Knoblauch, *ib.*, **43**. 738, 1891; E. Wiedemann, *ib.*, **32**. 452, 1887; G. Jäger and S. Meyer, *ib.*, **67**. 427, 707, 1899; G. van Pelt, *Bull. Soc. Chim. Belg.*, **28**. 101, 1914; H. W. Vogel, *Sitzber. Akad. Berlin*, 409, 1878; *Ber.*, **11**. 913, 1363, 1878; W. N. Hartley, *Trans. Roy. Soc. Dublin*, (2), **7**. 253, 1900; W. Lapraik, *Journ. prakt. Chem.*, (2), **47**. 305, 1893; S. M. Jörgensen, *ib.*, (2), **25**. 415, 1882; J. Formanek, *Die qualitative Spectralanalyse anorganischer und organischer Körper*, Berlin, 144, 1905; J. M. Hiebendaal, *Onderzoek over eenige absorptiespectra*, Utrecht, 1873; J. L. Soret, *Arch. Sciences Genève*, (2), **63**. 89, 1878; C. R. C. Tichborne, *Proc. Irish Acad.*, **1**. 169, 1874; *Chem. News*, **24**. 199, 209, 1871; H. M. Vernon, *ib.*, **66**. 104, 114, 141, 152, 1892; F. L. S. Jones, *Journ. Ind. Eng. Chem.*, **15**. 289, 1923; J. B. Elias, *Anal. Fis. Quim.*, **16**. 467, 1918; S. Aoyama, K. Kimura and Y. Nishina, *Zeit. Physik*, **44**. 810, 1927; A. E. Lindh, *ib.*, **6**. 303, 1921; L. R. Ingersoll, *Journ. Amer. Opt. Soc.*, **6**. 663, 1922; L. A. Welo, *Phil. Mag.*, (7), **6**. 481, 1928; L. Meunier and M. Lesbre, *Compt. Rend.*, **190**. 183, 1930; K. H. Gustavson, *Journ. Amer. Leather Chem. Assoc.*, **19**. 446, 1924; E. N. Gapon, *Journ. Russ. Phys. Chem. Soc.*, **58**. 1584, 1926; **60**. 237, 1928; **61**. 375, 1929; *Zeit. anorg. Chem.*, **168**. 125, 1927.

§ 23. The Chromium Oxychlorides

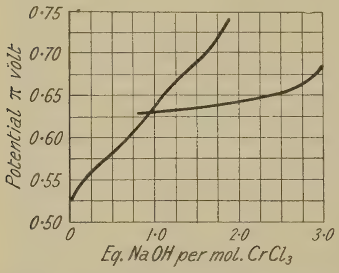


FIG. 77.—Electrometric Titration of Solutions of Chromic Chloride with Sodium Hydroxide.

The hydrolysis of chromic chloride, and the formation of some basic chlorides have just been discussed. N. Bjerrum[1] studied the titration of soln. of chromic chloride with sodium hydroxide, and calculated the $H^{\cdot}$-ion conc. from the potential measurements. The results with $0{\cdot}1M$-$CrCl_3$ and increasing proportions of $0{\cdot}1275M$-NaOH, at 17°, are illustrated by Fig. 77. When there is less than a mol of sodium hydroxide per mol of chromic chloride, the curve is steep, and the soln. remains clear; as soon as a mol of NaOH has been added, chromic hydroxide separates, and the soln. becomes turbid, and thereafter the $H^{\cdot}$-ion conc. increases slowly. So long as the soln. remains clear, the reaction is taken to be $Cr^{\cdots}+HOH=Cr(OH)^{\cdot\cdot}+H^{\cdot}$ for which the equilibrium constant $K_1=[Cr(OH)^{\cdot\cdot}][H^{\cdot}]/[Cr^{\cdots}]$, thereafter the reaction $Cr(OH)^{\cdot\cdot}+HOH=Cr(OH)_2{}^{\cdot}+H^{\cdot}$ sets in, and for this, $K_2[Cr(OH)_2{}^{\cdot}][H^{\cdot}]/[Cr(OH)^{\cdot\cdot}]$; and later on there is the reaction $Cr(OH)^{\cdot\cdot}+2H_2O=Cr(OH)_3+2H^{\cdot}$, for which $K_3=[H^{\cdot}]^2/[Cr(OH)^{\cdot\cdot}]$. He found for the hydrolysis constants of the green salt at 25°, $3{\cdot}8\times10^{-6}$; and of the blue salt at 0°, 17°, and 25°, $K_1\times10^4=0{\cdot}22$, 0·62, and 0·98 respectively; at 0° and 17°, $K_2\times10^4=0{\cdot}0025$ and 0·0059 respectively; and $K_3\times10^4=0{\cdot}278$ and 0·98 respectively. It is hence calculated that for $0{\cdot}01M$-$CrCl_3$ with the addition of x mols of $0{\cdot}1275N$-NaOH, the soln. contains the following proportions of the hydroxychlorides:

x . .	0	0·215	0·553	1·00	1·51	2·19	2·96
$CrCl_3$.	92·5	75·2	42·9	9·8	6·6	2·4	0
$Cr(OH)Cl_2$	7·5	22·9	52·3	74·9	57·3	29·2	1·2
$Cr(OH)_2Cl$	0	0·1	0·6	5·5	4·8	3·5	0·7
$Cr(OH)_3$.	0	0	0	2·4	20·5	50·0	78·9

It is also possible to calculate for the thermal values of these products $Cr(OH)Cl_2+HCl_{aq.}=CrCl_{3aq.}+H_2O+9600$ cals.; $Cr(OH)_2Cl+HCl_{aq.}=Cr(OH)Cl_2+H_2O+8060$ cals.; and $Cr(OH)_3+2HCl_{aq.}=Cr(OH)Cl_2+2H_2O+11{,}600$ cals. From the first and third equation, $Cr(OH)_3+3HCl_{aq.}=CrCl_{3aq.}+3H_2O+21{,}200$ cals., when A. Recoura found 20,700 cals. N. Bjerrum also added that it is probable that some polymerized basic chlorides exist. Observations on the electrometric titration of the chromic chlorides were also made by J. Sand and F. Grammling, who inferred from the potential of a hydrogen electrode, and the rate of liberation of iodine from an iodide-iodate mixture that the hydrolysis of the blue salt involves the breaking down of a doubled molecule: $Cr_2(H_2O)_{12}^{\cdot\cdot\cdot\cdot\cdot\cdot}+2H_2O\rightleftharpoons 2Cr(H_2O)_6OH^{\cdot\cdot}+2H^{\cdot}$, but N. Bjerrum did not agree. H. G. Denham obtained a value for the hydrolysis constant of the blue salt twice as great as N. Bjerrum. H. T. S. Britton found that with 0·0133*N*-soln. 1·62 per cent. of the violet, and 16·4 per cent. of the green salt was hydrolyzed at 18°. A. B. Lamb and G. R. Fonda calculated the hydrolysis constant of the green salt from conductivity data to be $1{\cdot}8\times10^{-6}$, and from the kinetics of the transformation $2{\cdot}0\times10^{-6}$. The hydrolysis constant for the violet salt calculated from the change of conductivity with conc. is $1{\cdot}52\times10^{-4}$; from the rate of transformation of the green salt, $1{\cdot}65\times10^{-4}$; from the rate of inversion of cane-sugar, $1{\cdot}60\times10^{-4}$; from the conductivity with or without the addition of hydrochloric acid, $1{\cdot}47\times10^{-4}$, and with the addition of sodium acetate, $1{\cdot}68\times10^{-4}$—mean value $1{\cdot}58\times10^{-4}$.

A number of basic chlorides have been reported by A. J. Béchamp and others, but their chemical individuality has not been established. A. Moberg, for example, said that $Cr_2O_3.8CrCl_3.24H_2O$ is formed by heating hydrated chromic chloride to 120°; H. Schiff regarded it as *chromic hydroxypentachloride*, $Cr_2Cl_5(OH).4H_2O$. By heating the hydrated salt to 150°, A. Moberg obtained $Cr_2O_3.4CrCl_3.9H_2O$, which H. Schiff regarded as *chromic dihydroxytetrachloride*, $Cr_2Cl_4(OH)_2.2H_2O$, or *chromium oxytetrachloride*, $Cr_2O.Cl_4.3H_2O$; E. M. Péligot obtained the same salt by heating the hydrated chloride to 200°, digesting the product with water, and drying it at 200°. H. Löwel obtained a similar product. B. Cabrera and S. P. de Rubies obtained the salt in green and violet modifications and studied their magnetic properties. V. Kletzinsky said that *chromic oxydichloride*, $Cr_4(OCl_2)_3$, is formed by evaporating to dryness a soln. of potassium chlorochromate in conc. hydrochloric acid. A. Moberg obtained *chromic oxychloride*, $Cr_2O_3.CrCl_3$, or $CrOCl$, by heating the hydrated chloride to dull redness. H. Schiff obtained the hydrate, $Cr_2O_3.CrCl_3.3H_2O$, or $CrCl(OH)_2$, *chromic dihydroxychloride*, by evaporating a soln. of chromic hydroxide in chromic chloride; and E. M. Péligot obtained a similar product from a mixture of a soln. of chromic chloride and alkali hydroxide. J. M. Ordway treated 6 mols of chromic hydroxide with 2 mols of hydrochloric acid and obtained $5Cr_2O_3.2CrCl_3$, which H. Schiff regarded as *chromic heptahydroxychloride*, $Cr_2(OH)_5Cl$. It was also obtained from a mixture of ammonia and a soln. of chromic chloride. A. Besson and L. Fournier heated a mixture of chromium trioxide and silicon hydrotrichloride in a sealed tube at 100°, and obtained a brown mass of *chromium oxyheptachloride*, Cr_3OCl_7. There are also N. Bjerrum's *chromic hydroxypentaquodichloride*, $[Cr(H_2O)_5(OH)]Cl_2$, and his *chromic dihydroxytetraquochloride*, $[Cr(H_2O)_4(OH)_2]Cl$, previously discussed.

R. F. Weinland and W. Friedrich[2] obtained what they called *pyridinium tetrachlorohydroxychromate*, $C_5H_5N.CrCl_4.OH,H_2O$, by the action of conc. hydrochloric acid and pyridine on chromic acid. The salt forms reddish-brown leaflets or orange-yellow, hexagonal plates. The analogous *quinolinium* compound was prepared. The interesting feature about these salts is that the chromium behaves as if it were quinquevalent, and the parent oxychloride is **chromium oxytetrachloride,** $CrOCl_3$. By saturating glacial acetic acid with hydrogen chloride, adding chromium trioxide, and then a soln. of alkali chloride in acetic acid soln., R. F. Weinland and M. Fiederer obtained **potassium chromium oxypentachloride,** $CrOCl_3.2KCl$, in dark garnet-red, rhombic prisms. The oxidizing power of the salt gradually diminishes when it is kept in a desiccator. The corresponding **rubidium chromium oxypentachloride,** $CrOCl_3.2RbCl$; **cæsium chromium oxypentachloride,** $CrOCl_3.2NH_4Cl$, are similarly prepared. The crystalline forms are similar to those of the corresponding salts of columbium and molybdenum. The cæsium salt is isomorphous with $CrOCl_3.2CsCl$. It was supposed that these products are salts of quinquevalent chromium, and a similar remark applies to various analogous compounds prepared by F. Olsson—*e.g.* $N(CH_3)_4CrOCl_4$; $N(C_2H_2)CrOCl_4$; etc.

J. J. Berzelius[3] discovered **chromium dioxydichloride,** or **chromyl chloride,** CrO_2Cl_2, which he obtained by distillation from a mixture of a chromate, sodium chloride, and conc. sulphuric acid. He thought that it was a higher chloride of chromium, but H. Rose proved that it contained oxygen. It was also analyzed by T. Thomson, P. Walter, and T. E. Thorpe, and these results, as well as the vap. density determinations of J. B. A. Dumas, P. Walter, E. Moles and L. Gomez, and E. Carstenjen; the f.p. determinations—*vide infra*—of R. E. Meyer and H. Best, and E. Moles and L. Gomez; and the b.p. determinations of E. Moles and L. Gomez, and G. Oddo and E. Serra are in agreement with the formula just indicated. The chromium is assumed to be sexivalent. E. R. Darling compiled a bibliography on the chemistry of chromyl chloride. G. Mazzaron said that the chlorides of silver, mercury, gold, and platinum, and antimony oxychloride give chlorine, not chromyl chloride when treated with potassium dichromate and sulphuric acid. F. Wöhler, A. Vogel, P. Walter, H. Rose, E. Burcker, E. Moles and L. Gomez, and G. Errera used modifications of this process: $3K_2CrO_4+6NaCl+12H_2SO_4=6KHSO_4+6NaHSO_4+3CrO_2Cl_2+6H_2O$. J. B. A. Dumas used lead chromate; potassium dichromate was used by T. Thomson. T. Thomson said that a better yield is obtained by using fuming sulphuric acid: $K_2Cr_2O_7+4NaCl+3H_2S_2O_7=2CrO_2Cl_2+K_2SO_4+2Na_2SO_4+3H_2SO_4$—but, added A. Étard, if the fuming acid be in excess, the chromyl chloride suffers some decomposition: $6CrO_2Cl_2+3H_2S_2O_7=2Cr_2(SO_4)_3+2CrO_3+6Cl_2+3H_2O$. H. Rose, and J. B. A. Dumas said that so much chlorine may be evolved that if the receiver is very cold, the product may solidify. P. Walter, and E. Carstanjen purified the liquid by fractional distillation for a number of times whereby the chlorine is given off first, and then the chromyl chloride, while sulphuric acid remains in the retort. T. E. Thorpe purified the liquid by fractional distillation in a current of carbon dioxide; and E. Moles and L. Gomez repeatedly fractioned the product after agitation with mercury. According to the Permutit A. G., an acid chloride, like chlorosulphonic acid, reacts with chromic acid or a chromate in the presence of conc. sulphuric acid or other diluting agent which does not decompose chromyl chloride; the acid anhydride—sulphur trioxide when chlorosulphonic acid is used—is converted into an acid chloride by the introduction of hydrochloric acid, and then acts on fresh chromic acid.

K. Heumann and P. Köchlin, and H. Moissan obtained chromyl chloride by the action of hydrogen chloride on dry chromium trioxide. W. Autenrieth treated chromium trioxide with 35 to 40 per cent. hydrochloric acid, and obtained a 35 per cent. yield of chromyl chloride, the yield is reduced with more dilute acid until with 20 per cent. hydrogen chloride, only chlorine is given off. H. Moissan also replaced the chromium trioxide with alkali or alkaline earth chromates; and moist chlorine can be used in place of hydrogen chloride at a temp. of 150°. L. Henry passed hydrogen chloride into sulphuric acid with chromium trioxide in suspension; and R. J. Meyer and H. Best suspended the chromium trioxide in glacial acetic acid; while H. D. Law and F. M. Perkin heated a soln. of chromium trioxide, conc. sulphuric acid, and conc. hydrochloric acid. A. Geuther chlorinated the chromium trioxide by heating it with anhydrous ferric or chromic chloride: $2FeCl_3+3CrO_3=Fe_2O_3+3CrO_2Cl_2$; H. Schiff, by phosphorus pentachloride; H. Erdmann, by chloroform: $2CHCl_3+CrO_3+O_2=2COCl_2+H_2O+CrO_2Cl_2$; A. Michael and A. Murphy, by carbon tetrachloride in a sealed tube at 150°–175°; and H. S. Fry, by acetyl chloride on a soln. of chromium trioxide in chloroform and acetic acid. A. Rosenstiehl treated chromates with pyrosulphuryl chloride; and K. Heumann and P. Köchlin used chlorosulphonic acid. E. M. Péligot treated potassium chlorochromate with sulphuric acid. H. Moissan found that moist chlorine attacks uncalcined chromic oxide at 440°, forming first chromic chloride which then reacts with the moisture forming chromyl chloride, and hydrogen chloride. The reaction is reversed at a higher temp. At 440°, also, oxygen acts on chromic chloride, forming chromyl chloride. P. Pascal found that chromyl chloride is formed by slowly heating pentachromyl hexachloride. F. G. Nunez prepared chromyl chloride of a high degree of purity for at. wt. determinations.

T. Thomson described chromyl chloride as a blood-red liquid which appears black by reflected light. G. J. Stoney and J. E. Reynolds found that chromyl chloride forms a yellowish-red vapour resembling nitrogen peroxide and E. Moles and L. Gomez observed that it freezes to form pale red, acicular crystals. T. Thomson gave 1·913 for the **specific gravity** of the liquid at 10°; P. Walter, 1·91 at 21°; T. E. Thorpe, 1·961 at 0°; 1·92 at 25°; and 1·7578 at the b.p. 115·9°; and E. Moles and L. Gomez, 2·0515 to 2·0528 at −47°/4°; 1·9582 to 1·9591 at 0°/4°; and 1·9113 to 1·9124 at 25°/4°. J. B. A. Dumas found the **vapour density** (air unity) to be 5·35 at 127° and 5·69 at 147°—when the theoretical value for CrO_2Cl_2 is 5·35; P. Walter found 5·9 at 143·7°; E. Carstanjen, 5·39 at 200°; and E. Moles and L. Gomez, 5·31 at 181°. Hence the vapour is not dissociated at these temp. T. E. Thorpe gave for the **thermal expansion** of unit vol. at 0° to v vols. at θ°, $v=1+0{\cdot}0_3958600\theta+0{\cdot}0_51073\theta^2+0{\cdot}0_81962\theta^3$. R. J. Meyer and H. Best found that the mol. wt., calculated from **the depression in the freezing point** of acetic acid, is 208 to 218—the theoretical value for CrO_2Cl_2 is 155. This shows that polymerization is taking place. E. Moles and L. Gomez found 175 to 189 with this solvent; 153 to 161 with phosphoryl chloride; 175·5 to 241 with nitrobenzene; 185 to 399 with ethylene dibromide; 91·8 to 97·8 with stannic bromide; and 193 to 215 with antimony pentachloride. Dil. soln. in nitrobenzene and ethylene dibromide show ionization, passing, with increasing concentration, into association. G. Oddo and A. Casalino found for 0·9694 and 2·4708 grms. of chromyl chloride in 100 grms. of the complex $SO_3.2POCl_3$ respectively 188 and 237 for the mol. wt.—theoretical 155. G. Oddo and E. Serra found from **the raising of the boiling point** of soln. in benzene, and carbon tetrachloride, mol. wts. between those required for the single and for the double molecule. E. Moles and L. Gomez obtained normal values when the results are corrected for the volatility of the solute—166·7 to 170·6 was obtained with carbon tetrachloride, and 164 to 172 with carbon disulphide. E. Beckmann gave 55·0 for the **ebulliscopic constant**—the mol. rise of the b.p.—of chromyl chloride when it is used as a solvent for mol. wt. determinations. E. Moles and L. Gomez gave −96·5° for the **melting point;** and for the **boiling point** P. Walter gave 118°; E. Carstanjen, 117·6° at 753 mm.; H. D. Law and F. M. Perkin, 118·5°–116°; T. E. Thorpe, 115·9° at 733 mm. and 116·8° at 760 mm.; and E. Moles and L. Gomez, 116·3° at 760 mm. The b.p., θ°, at different press., p mm., are:

p . .	232·3	338·0	424·0	525·0	645·8	750·8	763·1	839·1
B.p. .	79·4°	90·5°	97·4°	104·5°	111·0°	116·3	117·0°	120·4°

The data can be represented by $\theta=53{\cdot}63+0{\cdot}1271p-0{\cdot}000058p^2$. M. Berthelot found that the mol. **heat of soln.** in 100 parts of water at 8° is 16·67 Cals. The **absorption spectrum** of chromyl chloride was first examined by W. H. Miller, H. Mayer, B. Käbitz, R. Ritschl, and A. C. S. van Heel. G. J. Stoney and J. E. Reynolds found that the absorption spectrum shows orange yellow and green lines; they also observed that, excepting a small strip in the red, the vapour absorbs all the spectrum of a colourless flame. M. R. Read said that chromyl chloride imparts a pale white light to the colourless gas-flame; and F. Gottschalk and E. Drechsel added that if the vapour mixed with oxygen be passed into a non-luminous gas-flame, the colour is a paler violet than that imparted to the flame by potassium, and the flame spectrum shows three violet, eight green, one yellow, three orange-red, and two red lines. A. Cornu could not find any regularities in the spectral lines. According to B. Käbitz, liquid chromyl chloride absorbs the whole visible spectrum.

J. W. Hittorf, and E. Moles and L. Gomez found chromyl chloride to be a non-conductor of electricity. E. Moles and L. Gomez found that the mol. **electrical conductivity** is 5·05, 2·60, 1·38, and 0·96 mhos with soln. containing respectively 0·0323, 0·0724, 0·1398, and 0·2170 mol of CrO_2Cl_2 per litre of dried nitrobenzene at 25°. If the solvent is not thoroughly dried, the conductivity is two to five times as great, and it increases with time. The mol. conductivity decreases with increasing concentration, and the curves are parallel with those for the mol. wt. of chromyl chloride in the same solvent. P. Walden found the **dielectric constant** of the liquid to be 2·6 at 20°.

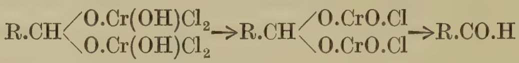
A. Étard said that chromyl chloride is very stable if it be protected from **light,** but in light it decomposes slowly forming chlorine and an oxide or oxychloride of chromium. F. Wöhler, and H. Quantin found that chromyl chloride is decomposed by **heat,** for when passed through a red-hot tube it furnishes crystals of chromic oxide: $2CrO_2Cl_2=Cr_2O_3+O+2Cl_2$; F. Wöhler, that a little above 300° it forms magnetic chromic chromate; and T. E. Thorpe, that at 180° to 190°, in a sealed tube, it forms chlorine and trichromyl chloride. If the vapour of chromyl chloride, mixed with dry **hydrogen,** be passed through a red-hot tube, A. Schafarik observed that it decomposes: $3CrO_2Cl_2+3H_2=6HCl+Cr_2O_3.CrO_3$; and when heated for a longer time, chromic oxide and oxygen are formed. F. Gottschalk and E. Drechsel said that a colourless gas-flame charged with a mixture of hydrogen and chromyl chloride becomes luminous, and deposits chromic oxide on a cold surface placed in the flame. J. B. A. Dumas, and P. Walter found that **water** decomposes chromyl chloride with the development of much heat forming a mixture of chromic and hydrochloric acids. J. J. Berzelius called the liquid *chlorwasserstoffsaure Chromsäure,* apparently regarding it as a special compound, for it was said to be formed by the action of hydrochloric acid on lead or silver chromate at the ordinary temp. The liquid is said to dissolve gold, and H. Moser found that when warmed chlorine is evolved. A. Étard, and J. B. A. Dumas observed that chromyl chloride absorbs **chlorine** freely, and becomes almost solid; H. W. B. Roozeboom found that the proportion of chlorine absorbed is dependent on the press. and temp. It increases rapidly as the temp. falls to —26° so that at 760 mm. press., a sat. soln. contains at 0°, 0·70 gram-atoms; at —14°, 1·24; at —21°, 2·31; and at —26°, 3·00. At 0°, the press., p mm., of soln. with N-gram-atoms of chlorine is:

Cl . . .	1·70	1·40	1·30	1·20	1·04	0·91
p . . .	1302	1198	1150	1101	1016	923 mm.

P. Walter said that chromyl chloride dissolves **iodine** without being decomposed; and R. W. E. McIvor said that when the mixture is distilled, iodine monochloride and trichromyl chloride are formed. H. Quantin found that dry **hydrogen chloride** reacts with chromyl chloride at a red-heat forming water, chlorine, and chromic oxide. J. B. A. Dumas found that **sulphur** decomposes chromyl chloride with a hissing noise; K. T. Kemp, and W. Gregory observed that a rose-coloured powder separates possibly chromic chloride; and T. Thomson added that when flowers of sulphur is moistened with it, the mixture ignites and burns with a red flame. K. T. Kemp found that if **hydrogen sulphide** be passed into chromyl chloride, the vessel becomes hot, hydrogen chloride is evolved, and a green powder is formed which A. Vogel said is probably chromic oxide. K. T. Kemp also found that if chromyl chloride vapour be passed through a narrow jet into the vapour of **sulphur monochloride,** vivid combustion occurs, and a rose-coloured powder is formed. K. Heumann and P. Köchlin observed that **chlorosulphonic acid** decomposes chromyl chloride; and, as indicated above, a similar remark applies to **pyrosulphuric acid.**

According to T. Thomson, chromyl chloride in **ammonia** solidifies with brilliant incandescence to form a dark brown mass, and with a more prolonged action on the residue, A. Schrötter, and C. E. Ufer found that chromium nitride or a mixture of nitride and oxide is formed. J. Heintze observed that with ammonia largely diluted by air, the residue, after washing, consists of chromic oxide. S. Rideal represented the reaction with dry ammonia, $3CrO_2Cl_2+8NH_3=6NH_4Cl+N_2+Cr_2O_3.CrO_3$. V. Thomas found that with **nitric oxide** and chromyl chloride vapour, a brown mass of **chromic dinitroxylheptoxypentachloride,** $Cr_5Cl_5O_7.2NO_2$, is formed; P. Pascal prepared pentitahexachloride by the action of nitric oxide—*vide infra.* J. B. A. Dumas, and P. Walter found that chromyl chloride explodes with **phosphorus,** and light is emitted at the same time—the effect is produced by a drop of the liquid and a piece of phosphorus the size of a pin's head. T. Thomson said that the phosphorus must be moistened to produce the explosion; when dry it is without action, and the flame of phosphorus is extinguished in the vapour of chromyl chloride. A. Michaelis observed that each drop of chromyl chloride added to well-cooled **phosphorus trichloride** produces a hissing noise, incandescence, and sometimes an explosion: $4CrO_2Cl_2+6PCl_3=4CrCl_3+3POCl_3+PCl_5+P_2O_5$. H. Schiff represented the reaction with **phosphorus pentachloride**: $2CrO_2Cl_2+4PCl_5=4POCl_3+3Cl_2+2CrCl_3$, and R. Weber, and A. W. Cronander added that some **chromium phosphoctochloride,** $CrCl_3.PCl_5$, is formed. H. S. Fry and J. L. Donnelly obtained the complex chromyl phosphoheptachloride, $CrO_2Cl_2.PCl_5$, by the action of chromyl chloride on a dry carbon tetrachloride soln. of phosphorus pentachloride. W. T. Casselmann showed that **phosphoryl chloride** reacts in the cold with chromyl chloride forming a black substance which decomposes at 100° as symbolized by $10POCl_3+12CrO_2Cl_2=18Cl_2+5P_2O_5+3Cr_2O_3+6CrCl_3$. E. Moles and L. Gomez found that chromyl chloride is soluble in phosphoryl chloride. H. S. Fry and J. L. Donnelly found that in soln. of dry carbon tetrachloride phosphorus trichloride reacts: $2CrO_2Cl_2+3PCl_3=PCl_5+2CrOCl.POCl_3$, and the deliquescent **chromium trioxyphosphotetrachloride** reacts with water: $CrOCl.POCl_3+2H_2O=CrCl_3+HCl+H_3PO_4$. On ignition, the complex **chromium trioxytrichloride,** CrOCl, or $Cr_2O_3.CrCl_3$ is formed. With **phosphorus tribromide, chromium trioxyphosphodichlorotribromide,** $2CrOCl.POBr_3$, is formed: $2CrO_2Cl_2+3PBr_3=2CrOCl.POBr_3+PBr_3Cl_2$. With **phosphorus pentabromide,** the complex **chromyl phosphodichloropentabromide,** $CrO_2Cl_2.PBr_5$, and **chromium dioxyphosphochlorotribromide,** $CrOCl.POBr_3$, are produced; with **phosphorus triiodide,** the complex **chromyl phosphodichlorotriiodide,** $CrO_2Cl_2.PI_3$, is formed, and it is decomposed by water: $2(CrO_2Cl_2.PI_3)+4H_2O=4HCl+4HI+I_2+2CrPO_4$; and with **phosphorus diodide,** the complex **chromyl phosphodichloridiiodide,** $CrO_2Cl_2.PI_2$ is formed: E. Moles and L. Gomez found that chromyl chloride is soluble in **antimony pentachloride,** and in **stannic bromide.**

J. B. A. Dumas, and T. Thomson found that **carbon** has no action on chromyl chloride. J. R. Mourelo and A. G. Banus found that the dried vapour of chromyl chloride mixed with air does not react: $4CrO_2Cl_2+4C+O_2=2Cr_2O_3+4COCl_2$, but chromic oxide is formed in the hot part of the tube and chromic chloride is deposited in the cooler part. It is difficult to get the charcoal free from hydrocarbons. The reaction of a mixture of chlorine and chromyl chloride with red-hot carbon is symbolized: $2CrO_2Cl_2+Cl_2+4C=2CrCl_3+4CO$. Chromyl chloride in general acts as an oxidizing and chlorinating agent on organic compounds: and in many cases the reaction is violent or explosive. H. Quantin found that when a mixture of the vapour of **carbon monoxide** and chromyl chloride is passed through a red-hot tube, chromic oxide and chloride are formed; and if the carbon monoxide be mixed with chlorine, and the temp. be 500° to 600°, carbon dioxide and chromic chloride are formed. P. Pascal obtained chromyl pentitahexachloride by reduction with carbon monoxide—*vide infra.* H. Erdmann, A. Emmerling and B. von Lengyel, and H. Quantin symbolized the reaction with **carbon tetrachloride**: $2CrO_2Cl_2+4CCl_4=2CrCl_3+4COCl_2+3Cl_2$. At ordinary temp. G. Oddo and E. Serra, and E. Moles and L. Gomez found it to be soluble in carbon tetrachloride; and R. J. Meyer and H. Best added that there is no action with carbon tetrachloride; and J. B. A. Dumas, none with **carbon disulphide,** and E. Moles and L. Gomez found that chromyl chloride dissolves in this liquid; and A. Étard found that in a sealed tube carbon disulphide reacts forming a complex mixture of products; and under similar conditions chloroform, with chromic acid and oxygen, furnishes carbonyl chloride, hydrogen chloride, and chromyl chloride; H. Erdmann, and A. Emmerling and B. von Lengyel represented the reaction: $2CHCl_3+CrO_3+O_2=2COCl_2+CrO_2Cl_2+H_2O$. F. Wöhler, and K. T. Kemp found that **ethylene** reacts forming ethylene chloride. E. Moles and L. Gomez found that it is soluble in **ethylene dibromide,** and in **nitrobenzene.** T. Thomson said that **turpentine** is inflamed by chromyl chloride, while **wood-spirit, camphor,** and **olive oil** are decomposed ; F. Wöhler found that **indigo** is not acted upon. F. Wöhler, P. Walter, and T. Thomson observed that with absolute **alcohol,** enough heat is generally evolved to produce combustion, and may be an explosion with violent projection of the liquids. R. J. Meyer and H. Best found that alcohol, **ether,** and **acetone** react with incandescence ; **benzene** is slowly attacked, but **toluene,** *o*-**xylene, pyridine,** and **quinoline** are vigorously attacked. A. Étard studied the reaction with **acetic acid** in a sealed tube at 100°, and obtained $Cr_2O_7\{Cr_2(C_2H_3O_2)_5\}_2.8H_2O$. E. Moles and L. Gomez studied soln. in acetic acid. The **aliphatic hydrocarbons,** $R.CH_3$, form the corresponding aldehyde, R.CO.H, with the formation of the intermediate compounds :



$$R.CH\begin{matrix}\diagup O.Cr(OH)Cl_2\\ \diagdown O.Cr(OH)Cl_2\end{matrix}\rightarrow R.CH\begin{matrix}\diagup O.CrO.Cl\\ \diagdown O.CrO.Cl\end{matrix}\rightarrow R.CO.H$$

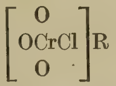
The reactions with aliphatic hydrocarbons, and various other organic compounds were studied by A. Étard, V. von Richter, P. Friedländer, E. Carstanjen, G. G. Henderson and co-workers, A. Haller, J. Bredt and W. Jagelki, D. Spence and J. C. Galletly, etc. Many of these reactions are discussed by G. Rohde, *Das Chromylchlorid und die Étard'sche Reaktion* (Stuttgart, 1901). J. B. A. Dumas, and P. Walter found that **mercury** is violently attacked by chromyl chloride.

According to E. Zettnow,[4] when chromyl chloride is distilled from a mixture of potassium chlorochromate and sulphuric acid, there is also formed a brown mass which is separated from the chromyl chloride, dissolved in water, and dried. Its composition corresponds with **chromyl tritadichloride,** $(CrO_2)_3Cl_2$. R. J. Meyer and H. Best represented it by the formula $Cl.CrO.O.CrO_2.O.CrO.Cl$. T. E. Thorpe made it by heating chromyl chloride in a sealed tube at 180° to 190° : $3CrO_2Cl_2=Cr_3O_6Cl_2+2Cl_2$; and R. W. E. McIvor, by distilling the iodine monochloride from a soln. of iodine in chromyl chloride : $3CrO_2Cl_2+2I_2=4ICl+Cr_2O_2Cl_2$. P. Pascal made it by heating chromyl pentitahexachloride. The black amorphous compound, said T. E. Thorpe, is reduced to chromic oxide when heated to a low temp. in hydrogen ; and R. W. E. McIvor obtained chromic oxide by heating it in air. According to T. E. Thorpe, and R. W. E. McIvor, when exposed to air the tritadichloride deliquesces to a reddish-brown syrup which smells of chlorine ; it is freely soluble in water forming a dark brown liquid which gives off chlorine ; a nitric acid soln. behaves as if it contained hypochlorous acid ; with hydrochloric acid, it forms a dark brown soln. which, when heated, gives off chlorine and forms chromic chloride ; with ammonia it forms ammonium chloride and chromate, and chromic chromate ; and, according to S. G. Rawson, it is scarcely soluble in carbon disulphide, but forms red soln. with alcohol, and ether.

According to P. Pascal, **chromyl pentitahexachloride,** $(CrO_2)_5Cl_6$, is formed when nitric oxide is passed into chromyl chloride, cooled in a bath of water ; heat is evolved and a crystalline paste is formed, nitrosyl chloride is evolved : $5CrO_2Cl_2+4NO=4NOCl+(CrO_2)_5Cl_6$, when the excess of chromyl chloride is removed, in vacuo at 100°, there remains the pentitahexachloride as a brown crystalline powder of sp. gr. 2·51. Carbon monoxide in sunlight can effect the same reduction as nitric oxide. Unlike chromyl chloride, the pentitahexachloride is strongly magnetic so that the function of chromium in the chromyl, CrO_2-radicle, and in the $(CrO_2)_5$-radicle appears to be different. In fact, chlorine, which acts only above 150°, slowly converts the pentitahexachloride back to chromyl chloride. Chromyl pentitahexachloride is deliquescent, and readily dissolves in water to a dark brown soln. with an odour of chlorine and the reactions of chromium salts, chromic acid, and hydrochloric acid. If slowly heated to 150°, chromyl chloride is evolved, and if quickly heated, chlorine only, the solid product in both cases being the tritadichloride, $(CrO_2)_3Cl_2$. Above 180° oxygen is evolved, leaving an insoluble brownish-black residue of $Cr_6O_9Cl_4$. Towards hydrogen, hydrogen sulphide, etc., chromyl subchloride acts as a chlorinating agent at low temp., whilst above 200° its action is generally an oxidizing as well as a chlorinating one. Moist gaseous ammonia acts very violently, the products being ammonium chloride, oxygen, and the oxides CrO_2 and Cr_2O_3. Generally speaking, however, chromyl pentitahexachloride is less reactive than chromyl chloride. When chromyl pentitahexachloride is suspended in dry ether, and a current of slightly moist ammonia is passed through, nitrogen is evolved, and ammonium chloride and a brown, amorphous precipitate remain. Ammonium chromate and chromium chromate are removed from the precipitate by washing, and the pale brown, insoluble residue when dried at 90° has the composition of an explosive *ammonium chromite*, $(NH_4O)_6(CrO_2)_5$.

According to G. Herfeldt,[5] if eq. proportions of chromium trioxide and chromyl chloride are heated in a sealed tube at 180°, impure **chlorochromic oxide,** $Cr_2O_5Cl_2$, or $(CrO_2Cl)_2O$, is formed. It is suggested that it is the anhydride, $CrO_2Cl–O–CrO_2Cl$, of the hypothetical *chlorochromic acid,* $HCrO_3Cl$, or $HO.CrO_2Cl$. The pale red compound is said to be very reactive, for it reacts explosively with alcohol, pyridine, and quinoline. A number of salts, **chlorochromates,** has been prepared. E. M. Péligot, and S. Löwenthal prepared **ammonium chlorochromate,** $(NH_4)CrO_3Cl$, as in the case of the potassium salt. It has the same appearance, but is much more soluble. S. Löwenthal prepared **lithium chlorochromate,** $LiCrO_3Cl$, from an aq. soln. of chromyl chloride and lithium chromate mixed with acetic acid. The yellowish-red crystals are, according to A. Fock, monoclinic; they are easily fused to a reddish-brown liquid; and are freely soluble in water. E. M. Péligot obtained **sodium chlorochromate,** $NaCrO_3Cl.2H_2O$, by adding sodium chloride to a conc. aq. soln. of chromyl chloride; G. Prätorius, by adding chromyl chloride to a conc. soln. of sodium carbonate in chromic acid, and allowing the mixture to stand some days in a desiccator over conc. sulphuric acid; and A. Ditte, by adding sodium chloride to a soln. of chromic acid. The dark reddish-yellow, prismatic crystals, when dried by press. between porous tiles lose water, and form an amorphous, yellow mass. If kept in a badly closed vessel, water of crystallization is taken up again. The compound melts by the heat of the hand, and at 110° loses chlorine, and water.

E. M. Péligot obtained **potassium chlorochromate,** $KCrO_3Cl$, by boiling potassium dichromate for a short time with an excess of hydrochloric acid, and cooling the liquid: $K_2Cr_2O_7+2HCl=H_2O+2KCrO_3Cl$—if boiled for too long a time some chromic acid is reduced; he also obtained it by mixing equimolar parts of potassium chloride and chromic acid in aq. soln., and adding hydrochloric acid—G. Herfeldt used a similar process. E. M. Péligot, and A. Werner, treated chromyl chloride with a sat. soln. of potassium chloride: $CrO_2Cl_2+KCl+H_2O=2HCl+KCrO_3Cl$; A. Ditte added potassium chloride to a hot soln. of an eq. quantity of chromic acid; A. Michaelis, by the action of phosphorus trichloride on potassium dichromate; A. Geuther added chromyl chloride to soln. of potassium chromate in dil. acetic acid: $K_2CrO_4+CrCl_2O_2=2KCrO_3Cl$; and also violet chromic chloride to molten potassium dichromate, $3K_2Cr_2O_7+2CrCl_3=Cr_2O_3+6KCrO_3Cl$. If the temp. is too high, chlorine may be given off. If the cold mass be dissolved in water acidified with acetic acid, and evaporated, the excess of potassium dichromate first separates out, and then follows the potassium chlorochromate. L. Varenne discussed the constitution of these salts, which are usually represented $RO.CrO_2.Cl$, or according to A. Werner's scheme:



$$\left[\begin{matrix}\mathrm{O}\\ \mathrm{OCrCl}\\ \mathrm{O}\end{matrix}\right]\mathrm{R}$$

E. M. Péligot said that the salt forms rectangular prisms, the colour of potassium dichromate; and that the salt is stable in air; A. Ditte found that the salt furnishes yellow needles which darken in air; and R. J. Meyer and H. Best, that when crystallized from acetic acid soln. over sulphuric acid, the salt is stable. G. N. Wyrouboff gave for the axial ratios of the monoclinic prisms $a:b:c=0·9653:1:1·0174$, and $\beta=90°\ 20'$. L. Playfair and J. P. Joule gave 2·49702 for the sp. gr. at 39°. J. Heintze, and J. G. Gentele said that when heated to 100°, the salt gives off chlorine; G. Herfeldt observed no evolution of chlorine below 250°, and he said that even after heating at 500° to 600° for some hours about 8 per cent. of chlorine remains in the residue. A. Streng also found that some oxygen is given off. A. Schafarik found that the salt readily fuses to a dark brown liquid with the evolution of chlorine and the formation of chromic oxide. A. C. Oudemans represented the reaction: $4KCrO_3Cl = K_2Cr_2O_7 + Cr_2O_3 + 2KCl + Cl_2 + O_2$; and A. Ditte noticed that a little chromyl chloride is also formed. F. Morges made some observations on the electrolysis of soln. of the salt. A. Ditte said that the salt is not decomposed when dissolved in water; and F. Morges gave 4·65 Cals. for the heat of soln. in 488 mols of water. E. M. Péligot found that the evaporation of the aq. soln. of the salt gives potassium dichromate; but with dil. hydrochloric acid the salt does not decompose; with conc. hydrochloric acid, potassium chloride, chromic chloride, and chlorine are formed. A. Ditte also noticed the evolution of chlorine when the salt is treated with hydrochloric acid. V. Kletzinsky observed that a violet mixture of potassium chloride and basic chromic chloride, $Cr_2O_3.2CrCl_3$—or possibly potassium chromium chloride, $KCrCl_4$—is formed by evaporating the soln. in conc. hydrochloric acid. E. M. Péligot found that with conc. sulphuric acid, chromyl chloride is evolved. H. Schiff gave for the reaction with fused potassium sulphate: $K_2SO_4 + KCrO_3Cl = KCl + KO.SO_2.O.CrO_2.OK$; and with potassium hydrosulphate; $KHSO_4 + KCrO_3Cl = HCl + KO.SO_2.O.CrO_2.OK$. J. Heintze observed that with ammonia, ammonium chloride, potassium chromochromate, etc., are formed, while A. Leist said that the products are potassium and ammonium dichromates, ammonium chloride, and chromic oxide. If the salt under ether, freed from moisture and alcohol, be treated with dry ammonia, chromium amidochromate is formed. A. Naumann found the salt to be soluble in acetone. J. Heintze said that the salt does not act on ether or benzene, but it oxidizes alcohol, and aniline; and a hot conc. soln. of potassium cyanide forms cyanogen chloride and potassium chromate.

E. M. Péligot reported **calcium chlorochromate,** $Ca(CrO_3Cl)_2.5H_2O$, to be formed as in the case of the potassium salt; but G. Prätorius could obtain it only by mixing 10 grms. of calcium carbonate or acetate with the theoretical quantity of solid chromium trioxide, forming 30 c.c. of acetic acid—containing an equal part of water and chromic acid—over the mixture and adding the calculated quantity of chromyl chloride. The reddish-yellow liquid is warmed on a water-bath, and the salt crystallizes out on cooling. The yellow, deliquescent salt melts in its water of crystallization at 56°. G. Prätorius obtained **strontium chlorochromate,** $Sr(CrO_3Cl)_2.4H_2O$, from an acetic acid soln. of strontium chromate, chromium trioxide and chromyl chloride. The carmine-red crystals melt without decomposition at 72°; they lose water when confined over sulphuric acid; and they form an orange liquid with water. Only impure, orange-yellow crystals of **barium chlorochromate** were prepared by G. Prätorius from glacial acetic acid soln. of barium chromate and chromyl chloride; but he obtained from the soln. a complex with acetic acid, **barium tetracetochlorochromate,** $Ba(CrO_3Cl)_2.4CH_3COOH.2H_2O$. He also obtained yellow crystals of **barium chlorochromatochloride,** $Ba(CrO_3Cl)Cl$, probably rhombic, from the mother-liquor remaining after the separation of the preceding salt, treated with conc. acetic acid on a water-bath. The hygroscopic crystals are freely soluble in water, and the yellow soln. when warmed deposits barium chromate; when the salt is heated, chromyl chloride is evolved. If the mother-liquor just indicated be acidified with dil. hydrochloric acid, yellow, six-sided plates of the *hydrate,* $Ba(CrO_3Cl)Cl.H_2O$, are formed. E. M. Péligot, and S. Löwenthal prepared **magnesium chlorochromate,** $Mg(CrO_3Cl)_2.9H_2O$, as in the case of the potassium salt, and G. Prätorius, from a soln. of magnesium carbonate in an excess of chromic acid and dil. hydrochloric acid. The reddish-yellow, hygroscopic, rhombic crystals melt in their water of crystallization at 66°; they form the *pentahydrate* when confined over sulphuric acid; and they lose chlorine and water at 135° to 140°. The salt is freely soluble in water. G. Prätorius prepared **zinc chlorochromate,** $Zn(CrO_3Cl)_2.9H_2O$, as in the case of the magnesium salt; and S. Löwenthal, from a cold, conc. soln. of zinc chloride and chromic acid acidified with acetic acid, and he dried the crystals on porous tiles. The reddish-yellow, hygroscopic, prismatic or tabular crystals decompose over sulphuric acid in a desiccator, giving off chlorine; they melt in their water of crystallization at 37·5°; they lose some water and chlorine at 100°. Chlorine is evolved when the salt is treated with lead oxide. M. Lachaud and C. Lepierre prepared impure **thallous chlorochromate,** $TlCrO_3Cl$, from a soln. of thallous chloride and chromic acid in a little water. The prismatic crystals are decomposed by water into thallous chloride and chromic acid. L. Bourgeois fused a mixture of lead chromate and chloride and obtained hexagonal prisms of **lead dichlorochromate,** $PbCl_2.PbCrO_4$. W. J. Sell prepared **chromic hexacarbamidochlorochromate,** $[Cr(CON_2H_4)_6](CrO_3Cl)_2.3H_2O$. G. Prätorius prepared hygroscopic, dark orange-yellow crystals of **cobalt chlorochromate,** $Co(CrO_3Cl)_2.9H_2O$, from a mixed soln. of chromic acid, cobalt carbonate and chromyl chloride. The crystals melt in their water of crystallization at 40° without decomposition; and they lose water on exposure to air. For **cobaltic hexamminochlorochromate,** $[Co(NH_3)_6]Cl(CrO_4).nH_2O$, *vide supra*, the chromates. The corresponding **nickel chlorochromate,** $Ni(CrO_3Cl)_2.9H_2O$, was obtained by G. Prätorius in a similar manner to the cobalt salt; the dark orange-yellow, hygroscopic crystals melt in their water of crystallization at 46° to 48°.

References.

[1] A. J. Béchamp, *Ann. Chim. Phys.*, (3), **56**. 306, 1859; (3), **57**. 296, 1859; V. Kletzinsky, *Zeit. Chem.*, (2), **2**. 127, 1866; *Mitteilungen aus dem Gebiete der reinen und angwandten Chemie*, Wien, 1865; H. Schiff, *Liebig's Ann.*, **124**. 172, 1862; A. Recoura, *Compt. Rend.*, **100**. 1227, 1886; **102**. 515, 922, 1886; *Recherches sur les chlorures de chrome*, Paris, 1886; *Ann. Chim. Phys.*, (6), **10**. 22, 1887; H. T. S. Britton, *Journ. Chem. Soc.*, **127**. 2110, 1925; J. Sand and F. Grammling, *Zeit. phys. Chem.*, **62**. 1, 28, 1908; A. Moberg, *Dissertatio de chloreto chromoso*, Helsingfors, 1843; *Journ. prakt. Chem.*, (1), **29**. 175, 1843; (1), **44**. 322, 1848; H. G. Denham, *Journ. Chem. Soc.*, **93**. 53, 1908; A. B. Lamb and G. R. Fonda, *Journ. Amer. Chem. Soc.*, **43**. 1154, 1921; H. Löwel, *Journ. Pharm. Chim.*, (3), **4**. 401, 1845; E. M. Péligot, *Compt. Rend.*, **21**. 24, 1845; A. Besson and L. Fournier, *ib.*, **148**. 1192, 1909; B. Cabrera and S. P. de Rubies, *Anal. Fis. Quim.*, **17**. 149, 1919; J. M. Ordway, *Amer. Journ. Science*, (2), **26**. 203, 1858; N. Bjerrum, *Danske Selsk. Skr.*, **4**. 1, 1906; *Zeit. phys. Chem.*, **59**. 336, 581, 1907; **73**. 724, 1910.

[2] R. F. Weinland and W. Friedrich, *Ber.*, **38**. 3784, 1905; R. F. Weinland and M. Fiederer, *ib.*, **39**. 4042, 1906; **40**. 2090, 1907; F. Olsson, *Arkiv Kemi Min. Geol.*, **9**. 10, 1924.

[3] H. D. Law and F. M. Perkin, *Journ. Chem. Soc.*, **91**. 191, 1907; T. E. Thorpe, *ib.*, **21**. 514, 1868; **37**. 362, 1880; S. Rideal, *ib.*, **49**. 367, 1886; G. G. Henderson and R. W. Smith, *ib.*, **55**. 45, 1889; G. G. Henderson and T. Gray, *ib.*, **83**. 1301, 1903; G. G. Henderson, *ib.*, **91**. 1871, 1907; G. G. Henderson and J. M. Campbell, *ib.*, **57**. 253, 1890; K. Heumann and P. Köchlin, *Ber.*, **15**. 1115, 1882; W. Autenrieth, *ib.*, **35**. 2064, 1902; H. Erdmann, *Liebig's Ann.*, **362**. 148, 1908; *Ber.*, **26**. 1992, 1893; P. Friedländer, *ib.*, **28**. 1387, 1895; V. von Richter, *ib.*, **19**. 1062, 1886; A. Cornu, *Journ. Phys.* (1), **1**. 63, 1872; G. J. Stoney and J. E. Reynolds, *B.A. Rep.*, 434, 1878; *Phil. Mag.*, (4), **41**. 291, 1871; (4), **42**. 41, 1871; W. H. Miller, *ib.*, (3), **2**. 381, 1833; A. Michaelis, *Jena Zeit.*, **7**. 110, 1871; A. C. S. van Heel, *Proc. Amsterdam Acad.*, **30**. 95, 1927; *Versl. Amsterdam Acad.*, **35**. 1112, 1926; A. Vogel, *Repert. Pharm.*, **11**. 184, 1863; R. Ritschl, *Zeit. Physik*, **42**. 172, 1927; Permutit A. G., *Brit. Pat. No.* 270711, 1927; H. W. B. Roozeboom, *Rec. Trav. Chim. Pays-Bas*, **4**. 379, 1886; K. T. Kemp, *Pharm. Journ.*, (2), **20**. 413, 1834; A. Schafarik, *Sitzber. Akad. Wien*, **47**. 255, 1863; E. R. Darling, *Chem. Met. Engg.*, **26**. 59, 1922; P. Walden, *Zeit. Phys. Chem.*, **46**. 180, 1903; E. Moles and L. Gomez, *ib.*, **80**. 513, 1912; **90**. 594, 1915; *Anal. Fis. Quim.*, **10**. 43, 1912; J. R. Mourelo and A. G. Banus, *ib.*, **8**. 355, 1910; M. R. Read, *Chem. News*, **95**. 169, 1907; R. W. E. McIvor, *ib.*, **28**. 138, 1873; G. Rohde, *Das Chromylchlorid und die Étard'sche Reaktion*, Stuttgart, 1901; A. Michael and A. Murphy, *Amer. Chem. Journ.*, **44**. 379, 1910; H. S. Fry, *Journ. Amer. Chem. Soc.*, **33**. 698, 1911; H. S. Fry and J. L. Donnelly, *ib.*, **38**. 1923, 1916; **40**. 478, 1918; D. Spence and J. C. Galletly, *ib.*, **33**. 190, 1911; H. Moser, *Chemische Abhandlung über das Chrom*, Wien, 1924; *Schweigger's Journ.*, **42**. 99, 1924; G. Mazzaron, *Atti Ist. Venezia*, (7), **7**. 1124, 1896; A. Emmerling and B. von Lengyel, *Zeit. Chem.*, (2), **7**. 101, 1871; O. Unverdorben, *Trommsdorff's Journ.*, **9**. 26, 1824; *Pogg. Ann.*, **7**. 311, 1826; H. Rose, *ib.*, **27**. 573, 1833; **45**. 183, 1838; J. J. Berzelius, *ib.*, **1**. 34, 1824; F. Wöhler, *Gött. Nachr.*, 147, 1859; *Ann. Chim. Phys.*, (3), **56**. 501, 1859; *Liebig's Ann.*, **13**. 297, 1828; **33**. 343, 1834; **111**. 117, 1859; J. W. Hittorf, *ib.*, **106**. 566, 1859; R. Weber, *ib.*, 386, 1859;

J. von Liebig, *ib.*, **21**. 359, 1837 ; T. Thomson, *Phil. Trans.*, **117**. 195, 1827 ; *Phil. Mag.*, (2), **1**. 452, 1827 ; A. Geuther, *Liebig's Ann.*, **106**. 239, 1858 ; **118**. 69, 1861 ; H. Schiff, *ib.*, **102**. 111, 1857 ; **106**. 116, 1858 ; W. T. Casselmann, *ib.*, **98**. 213, 1856 ; J. Bredt and W. Jagelki, *ib.*, **310**. 119, 1900 ; A. Schrötter, *ib.*, **37**. 148, 1841 ; C. E. Ufer, *ib.*, **112**. 281, 1859 ; E. Carstanjen, *Journ. prakt. Chem.*, (1), **107**. 331, 1869 ; (2), **2**. 52, 1870 ; F. Gottschalk and E. Drechsel, *ib.*, (1), **89**. 473, 1863 ; J. Heintze, *ib.*, (2), **4**. 219, 1871 ; W. Gregory, *ib.*, (1), **3**. 52, 1834 ; *Journ. Pharm. Chim.*, (2), **20**. 413, 1834 ; L. Henry, *Bull. Acad. Belg.*, (2), **21**. 233, 1866 ; R. J. Meyer and H. Best, *Zeit. anorg. Chem.*, **22**. 192, 1899 ; E. Beckmann, *ib.*, **77**. 90, 1912 ; H. Moissan, *Bull. Soc. Chim.*, (2), **43**. 6, 1884 ; *Compt. Rend.*, **90**. 1357, 1880 ; **98**. 1581, 1884 ; *Ann. Chim. Phys.*, (5), **21**. 246, 1880 ; (6), **5**. 571, 1885 ; E. M. Péligot, *ib.*, (2), **52**. 272, 1833 ; J. Persoz, *ib.*, (2), **44**. 315, 1830 ; P. Walter, *Compt. Rend.*, **5**. 753, 1837 ; *Ann. Chim. Phys.*, (2), **66**. 387, 1837 ; J. B. A. Dumas, *ib.*, (2), **31**. 435, 1826 ; A. Étard, *Compt. Rend.*, **84**. 127, 391, 614, 951, 1877 ; **87**. 989, 1878 ; **90**. 534, 1880 ; **97**. 909, 1883 ; **116**. 434, 1893 ; **120**. 1058, 1895 ; *Bull. Soc. Chim.*, (2), **27**. 249, 1877 ; (2), **28**. 275, 1877 ; *Recherches sur le rôle oxydant de l'acide chlorochromique*, Paris, 1880 ; *Ann. Chim. Phys.*, (5), **22**. 221, 1887 ; E. Burcker, *ib.*, (5), **26**. 433, 1882 ; M. Berthelot, *ib.*, (6), **1**. 93, 1884 ; *Compt. Rend.*, **96**. 400, 1883 ; H. Quantin, *ib.*, **99**. 709, 1884 ; **104**. 223, 1887 ; V. Thomas, *ib.*, **129**. 828, 1899 ; A. Rosenstiehl, *ib.*, **53**. 659, 1861 ; A. Haller, *ib.*, **84**. 558, 703, 1877 ; P. Pascal, *ib.*, **148**. 1443, 1909 ; G. Errera, *Gazz. Chim. Ital.*, **21**. i, 77, 1891 ; G. Oddo and E. Serra, *ib.*, **29**. ii, 318, 1899 ; G. Oddo and A. Casalino, *ib.*, **57**. i, 60, 1927 ; B. Käbitz, *Ueber die Absorptionsspectra der Chlorsäuren*, Bonn, 1905 ; H. Mayer, *Zeit. phys. Chem.*, **113**. 220, 1924 ; A. W. Cronander, *Ber.*, **6**. 1466, 1873 ; *Bull. Soc. Chim.*, (2), **19**. 499, 1873 ; *Oefvers. Akad. Stockholm*, **27**. 57, 1870 ; F. G. Nunez, *Anal. Fis. Quim.*, **28**. 579, 1930.

[4] T. E. Thorpe, *Journ. Chem. Soc.*, **23**. 31, 1870 ; R. W. E. McIvor, *Chem. News*, **28**. 138, 1873 ; S. G. Rawson, *ib.*, **59**. 185, 1889 ; P. Pascal, *Compt. Rend.*, **148**. 1463, 1909 ; R. J. Meyer and H. Best, *Zeit. anorg. Chem.*, **22**. 194, 1899 ; E. Zettnow, *Pogg. Ann.*, **143**. 328, 1871 ; R. J. Meyer and H. Best, *Zeit. anorg. Chem.* **22**. 192, 1899.

[5] E. M. Péligot, *Ann. Chim. Phys.*, (2), 272, 1833 ; J. Heintze, *Journ. prakt. Chem.*, (2), **4**. 219, 1871 ; G. Herfeldt, *ib.*, (2), **50**. 94, 1894 ; A. Leist, *ib.*, (2), **5**. 332, 1872 ; A. Michaelis, *ib.*, (2), **4**. 449, 1897 ; A. Geuther, *Liebig's Ann.*, **106**. 240, 1858 ; **118**. 68, 1861 ; A. Streng, *ib.*, **129**. 227, 1864 ; H. Schiff, *ib.*, **126**. 171, 1863 ; G. Prätorius, *ib.*, **201**. 16, 1880 ; *Ueber die Salze der Chlorchromsäure*, Tübingen, 1878 ; S. Löwenthal, *Zur Kenntnis der chlor- und amidochromsauren Salze*, Rostock, 1893 ; *Zeit. anorg. Chem.*, **6**. 357, 1894 ; R. J. Meyer and H. Best, *ib.*, **22**. 196, 1899 ; A. Werner, *ib.*, **9**. 407, 1895 ; A. Fock, *Zeit. Kryst.*, **23**. 217, 1894 ; A. Naumann, *Ber.*, **37**. 4328, 1904 ; A. Ditte, *Compt. Rend.*, **134**. 337, 1902 ; F. Morges, *ib.*, **86**. 1445, 1878 ; **87**. 15, 1878 ; L. Varenne, *ib.*, **93**. 730, 1881 ; M. Lachaud and C. Lepierre, *ib.*, **103**. 198, 1891 ; A. C. Oudemans, *Rec. Trav. Chim. Pays-Bas.*, **5**. 111, 1886 ; A. Schafarik, *Sitzber. Akad. Wien*, **47**. 253, 1863 ; G. N. Wyrouboff, *Bull. Soc. Chim.*, (3), **11**. 850, 1894 ; *Bull. Soc. Min.*, **3**. 143, 1880 ; L. Bourgeois, *ib.*, **10**. 188, 1887 ; J. G. Gentele, *Dingler's Journ.*, **125**. 452, 1861 ; L. Playfair and J. P. Joule, *Mem. Chem. Soc.*, **2**. 401, 1845 ; *Journ. Chem. Soc.*, **1**. 137, 1849 ; V. Kletzinsky, *Zeit. Chem.*, (2), **2**. 127, 1866 ; *Mitteilungen aus dem Gebiete der reinen und angewandten Chemie*, Wien, 1865 ; W. J. Sell, *Proc. Roy. Soc.*, **45**. 321, 1889.

§ 24. The Chromium Ammines

The ammines of chromium were first obtained by E. Frémy [1] in 1858, and they were soon afterwards studied by P. T. Cleve, and then by J. Morland, A. Reinecke, and S. M. Jörgensen. A. Werner showed that as in the case of the cobalt, and platinum ammines, most of the chromium ammines fitted into the system based on his co-ordination theory—**8**. 49, 19. I. I. Chernyeff studied the inner structure of the chromium ammines. Extensive investigations on the chromium ammines have been made by P. Pfeiffer and his fellow-workers, and the following summary is based on his reports :

A.—Compounds with one chromium atom in the nucleus.

I.—**The hexammine family,** or compounds of the tervalent basic group : $[CrA_6]'''$.

(i) *Hexammines*, $[Cr(NH_3)_6]X_3$. These salts are the so-called *chromium luteosalts*, studied by S. M. Jörgensen, A. Benrath, O. T. Christensen, W. R. Lang and C. M. Carson, J. Meyer and L. Speich, H. J. S. King, P. Pfeiffer and S. Basci, L. A. Welo, and P. Pfeiffer and M. Haimann, J. Petersen, O. Stelling, O. Hassel and G. B. Næss, E. Wilke-Dörfurt and co-workers, and A. Werner and A. Miolati. These salts include : (1) chloride and (2) its mercurichloride, and (3) chloroplatinate ; (4) bromide and (5) its bromoplatinate ; (6) iodide, and (7*a*) its sulphate, and (7*b*) selenate; (8) perchlorate; (9) sulphate and (10) its chloroplatinate; (11) nitrate and (12) its chloroplatinate; (13) dinitratofluosulphonate; (14) phosphate and (15) its sodiopyrophosphate; (16) oxalate and (17) its chromioxalate, (18) its cobaltioxalate; (19) cyanide and (20) its chromicyanide, (21) its ferricyanide; (22) its cobalticyanide; (23) picrate; (24) dipicrylamide; (25) 2 : 4-dinitro-α-naphthoxide; (26) 2 : 4-dinitro-α-naphthoxide-γ-sulphonate; (27) 2 : 3 : 6-trinitrophenoxide; (28) 1 : 2-naphthaquinone-1-oximate (1-nitroso-β-naphthoxide); (29) 1 : 2-dihydroxyanthraquinone; (30) picramate, and (31) permanganate.

(ii) *Trisethylenediamines*, $[\mathrm{Cr\,en_3}]X_3$. These salts were studied by J. Meyer and L. Speich, L. A. Welo, P. Pfeiffer, P. Pfeiffer and A. Trieschmann, P. Pfeiffer and M. Haimann, and A. G. Berghman. They include: (1) chloride; (2) bromide; (3) iodide; (4) nitrate; (5) selenate; (6) oxalate, and (7) its chromioxalate, and (8) cobaltic oxalate; (9) cyanide, and (10) its chromicyanide, and (11) cobalticyanide; (12) thiocyanate, and (13) its chromithiocyanate; and (14) dichromate.

(iii) *Hexacarbamides*, or *hexaurea salts*, $[\mathrm{Cr(NH_2.CO.NH_2)_6}]X_3$. W. J. Sell, M. Kilpatrick, P. Pfeiffer, A. Werner and D. Kalkmann, G. A. Barbieri, and J. Meyer and L. Speich, E. Wilke-Dörfurt and co-workers studied these salts, and reported: (1) the chloride, and its complex (2) with mercuric chloride, and (3) with platinic chloride; (4) bromide; (5) perbromide; (6) iodide; (7) periodide; (8) chlorate; (9) perchlorate; (10) hexasulphide; (11) sulphate; (12) hydrosulphate; (13) chlorosulphate; (14) bromosulphate; (15) perbromosulphate; (16) iodosulphate; (17) periodosulphate; (18) chloratosulphate; (19) perchlorate; (20) perchloratosulphate; (21) persulphate; (22) fluosulphonate; (23) sulphatofluosulphonate; (24) thiosulphate; (25) selenate; (26) periodocarbonate; (27) nitrite; (28) sulphatonitrite; (29) cobaltinitrite; (30) diamminotetranitritocobaltiate; (31) chlorodiamminotetranitritocobaltiate; (32) nitrate; (33) sulphatonitrate; (34) cyanide; (35) thiocyanate; (36) ferrocyanide; (37) ferricyanide; (38) nitroprusside; (39) manganicyanide; (40) cobalticyanide; (41) chloronickelocyanide; (42) chloroplatinocyanide; (43) hexathiocyanatochromiate; (44) hexacyanochromiate; (45) fluosilicate; (46) fluoborate; (47) fluoboratosulphate; (48) chromate; (49) chlorochromate; (50) dichromate; (51) chlorodichromate; (52) bromodichromate; (53) perchloratodichromate; (54) disulphatodichromate; (55) nitratodichromate; (56) tetrafluoboratodichromate; (57) permanganate; (58) sulphatopermanganate; (59) dichromatopermanganate; (60) oxalate; (61) picrate; (62) naphthalene-2-sulphonate; (63) toluenesulphonate; (64) *o*-dichlorobenzenesulphonate; (65) sulphatobenzenesulphonate; and (66) diflavianate-flavianate. E. Wilke-Dörfurt and R. Pfau studied the isomorphism of the permanganate, perchlorate, fluoborate, fluosulphonate, and iodide.

(iv) *Bisethylenediaminopropylenediamines*, $[\mathrm{Cr\,en_2pn}]X_3$. These salts were studied by P. Pfeiffer, P. Pfeiffer and H. Pietsch, and P. Pfeiffer, T. Gassmann. They include: (1) bromide; (2) iodide; (3) oxalate and (4) its chromioxalate, and (5) cobaltioxalate; (6) cyanide, and its (7) chromicyanide, and (8) cobalticyanide; and (9) thiocyanate.

(v) *Trispropylenediamines*, $[\mathrm{Cr\,pn_3}]X_3$. These salts were studied by P. Pfeiffer and M. Haimann, and P. Pfeiffer and T. Gassmann. They include: (1) iodide; (2) cobaltioxalate; (3) chromicyanide; (4) cobalticyanide; (5) thiocyanate; and (6) chromithiocyanate.

(vi) *Aquopentammines*, $[\mathrm{Cr(NH_3)_5(H_2O)}]X_3$. These salts are the so-called *chromium roseo-salts,* studied by S. M. Jörgensen, F. Ephraim and W. Ritter, A. Benrath, O. Hassel and G. B. Næss, A. Hiendlmayr, and O. T. Christensen. They include: (1) hydroxide; (2) fluoride—*vide supra,* (3) chloride, and (4) its mercurichloride; (5) bromide, and (6) its bromoplatinate; (7) iodide; (8) perchlorate; (9) sulphate, and (10) its chloroplatinate; (11) nitrate, and (12) hydronitrate; (13) cyanide, and (14) its chromicyanide, (15) its ferricyanide, and (16) its cobalticyanide. H. J. S. King showed that these salts may be hydroxypentammines.

(vii) *Diaquotetrammines,* $[Cr(NH_3)_4(H_2O)_2]X_3$. These salts were investigated by P. Pfeiffer. They include: (1) hydronitrate; (2) chloride; and (3) bromide.

(viii) *Diaquobisethylenediamines,* $[Cr\,en_2(H_2O)_2]X_3$. These salts were studied by P. Pfeiffer. These are the isomeric forms:

(*a*) *Cis-salts,* including (1) chloride; (2) bromide; (3) chromioxalate; and (4) chromithiocyanate.

(*b*) *Trans-salts,* including (1) chloride; and (2) bromide.

(ix) *Triaquotriammines,* $[Cr(NH_3)_3(H_2O)_3]X_3$. These salts were studied by A. Werner, S. Guralsky, and E. H. Riesenfeld and F. Seemann and they include: (1) the chloride; (2) the perchlorate; (3) the bromide; (4) hydroxyiodide; and (5) chloronitrate.

(x) *Tetraquodiammines,* $[Cr(NH_3)_2(H_2O)_4]X_3$. These salts were studied by A. Werner and J. Klein. They include: (1) chloride; (2) bromide; (3) sulphate.

(xi) *Tetraquodipyridines,* $[Crpy_2(H_2O)_4]X_3$. These salts were studied by P. Pfeiffer, P. Pfeiffer and W. Osann, and P. Pfeiffer and M. Tapuach. They include: (1) chloride; (2) bromide; (3) sulphate, and (4) hydrosulphate; (5) nitrate; and (6) chromicyanide.

(xii) *Diaquotetramido-salts,* $[Cr(H_2O)_2(C_2H_5O_2N)_4]$, studied by G. Florence and E. Couture.

(xiii) *Hexaquo-salts,* $[Cr(H_2O)_6]X_3$. These salts were studied by A. Werner and A. Gubser, A. Gubser, A. Werner and R. Huber, P. Pfeiffer, R. F. Weinland and R. Krebs, R. F. Weinland and T. Schumann, and L. A. Welo. They correspond with the hexahydrated chlorides, sulphates, and chlorosulphates. J. Meyer and L. Speich prepared the selenate.

(xiv) *Hexa-antipyrino-salts,* $[Cr(COC_{10}H_{12}N_2)_6]X_3$, were prepared by E. Wilke-Dörfurt and H. G. Mureck. For example, (1) the fluoborate, $[Cr(COC_{10}H_{12}N_2)_6](BF_4)_3$; (2) the permanganate; (3) the fluosulphonate; (4) the thiocyanate; (5) the dichromate; (6) the chlorate; (7) the thiosulphate; (8) the ferrocyanide; (9) the ferricyanide; and (10) the picrate.

(xv) *Trioxalato-salts,* $R_3'[Cr(C_2O_4)_3]$, studied by A. G. Berghman.

II.—**The pentammine family,** or compounds of the bivalent, basic group: $[CrA_5X]''$. P. Larisch made some comparative observations on the solubilities of these salts.

(i) *Hydroxypentammines,* $[Cr(NH_3)_5(OH)]X_2$. S. M. Jörgensen, P. Pfeiffer, A. Werner, A. Benrath, L. A. Welo, J. V. Dubsky, and H. J. S. King reported (1) chloride; (2) bromide; (3) iodide; (4) sulphate; (5) dithionate; (6) nitrate; (7) chromate; (8) oxalate; (9) picramate; (10) picrate; (11) dipicrylamide; and (12) 2 : 4-dinitro-α-naphthoxide-γ-sulphonate. The (13) hydroxide was obtained by the action of silver oxide on the chloride.

(ii) *Hydroxyaquopentammines,* $[Cr(NH_3)_5(H_2O)(HO)]X_2$. These salts were studied by P. Pfeiffer. They include: (1) bromide; and (2) dithionate.

(iii) *Hydroxyaquobisethylenediamines*, $[Cr\ en_2(H_2O)(HO)]X_2$. These salts were studied by P. Pfeiffer, P. Pfeiffer and R. Stern, P. Pfeiffer and R. Prade, P. Pfeiffer and T. G. Lando. There are isomeric forms:

(*a*) *Cis-salts*, including (1) chloride; (2) bromide; (3) iodide; and (4) dithionate.

(*b*) *Trans-salts*, including (1) bromide; (2) iodide and (3) dithionate.

(iv) *Hydroxydiaquotriammines*, $[Cr(NH_3)_3(H_2O)_2(HO)]X_2$ The iodide was studied by A. Werner.

(v) *Hydroxytriaquodiammines*, $[Cr(NH_3)_2(H_2O)_3(OH)]X_2$. The sulphate was studied by A. Werner and J. Klein, and A. Werner and V. Dubsky.

(vi) *Hydroxytriaquodipyridines*, $[Crpy_2(H_2O)_3(OH)]X_2$. These salts were studied by P. Pfeiffer, P. Pfeiffer and M. Tapuach, and P. Pfeiffer and W. Osann. They include: (1) chloride; (2) sulphate; and (3) thiocyanate.

(vii) *Nitritopentammines*, $[Cr(NH_3)_5(NO_2)]X_2$. They are the so-called *chromium xantho-salts*. These salts were studied by O. T. Christensen, J. N. Brönsted and A. Petersen, and A. Werner and A. Miolati. They include: (1) chloride, and (2) its mercurichloride, and (3) its chloroplatinate; (4) bromide; (5) iodide; (6) sulphate; (7) dithionate; (8) nitrate; (9) carbonate; (10) chromate; and (11) dichromate.

(viii) *Nitratopentammines*, $[Cr(NH_3)_5(NO_3)]X_2$. These salts were studied by A. Werner and J. von Halban. They include: (1) iodide and (2) nitrate.

(ix) *Nitratodiaquotriammines*, $[Cr(NH_3)_3(H_2O)_2(NO_3)]X_2$. The nitrate was studied by E. H. Riesenfeld and F. Seemann.

(x) *Fluopentammines*, $[Cr(NH_3)_5F]X_2$. These salts were prepared by A. Hiendlmayr. They include: (1) fluoride; (2) chloride; (3) nitrate; (4) chromate; and (5) ferricyanide.

(xi) *Chloropentammines*, $[Cr(NH_3)_5Cl]X_2$. These are the so-called *chromium purpureo-salts*. They were studied by O. T. Christensen, A. Werner and A. Miolati, O. Hassel and G. B. Næss, F. Ephraim and W. Ritter, J. Meyer and L. Speich, J. N. Brönsted and A. Petersen, H. J. S. King, L. A. Welo, and S. M. Jörgensen. They include: (1) chloride; (2) its mercurichloride, and (3) its chloroplatinate; (4) bromide, and (5) its mercuribromide; (6) iodide, and (7) its mercuriiodide; (8) chlorate; (9) perchlorate; (10) pentasulphide; (11) sulphate, and (12*a*) its hydrosulphate; (12*b*) selenate; (13) dithionate; (14) fluosilicate; (15) oxalate; (16) ferrocyanide; (17) chromate; (18) picrate; (19) 2 : 4-dinitro-α-naphthoxide; (20) 2 : 4-dinitro-α-naphthoxide-γ-sulphonate; and (21) 2 : 3 : 6-trinitrophenoxide.

(xii) *Chloroaquotetrammines*, $[Cr(NH_3)_4(H_2O)Cl]X_2$. These are the so-called *chromium roseo-salts*. They were studied by E. Frémy, P. T. Cleve, A. Werner and A. Miolati, S. M. Jörgensen, J. Petersen, P. Pfeiffer and S. Basci, P. Pfeiffer. They include: (1) chloride, and its (2) mercurichloride, and (3) its chloroplatinate; (4) bromide; (5) iodide; (6) sulphate; (7) nitrate; (8) fluosilicate; (9) oxalate; and (10) chromate.

(xiii) *Chlorodiaquotriammines*, $[Cr(NH_3)_3(H_2O)_2Cl]X_2$. These salts were studied by E. H. Riesenfeld and F. Seemann. They include: (1) chloride; and (2) sulphate.

(xiv) *Bromodiaquotriammines*, $[Cr(NH_3)_3(H_2O)_2Br]X_2$. These salts, prepared by S. Guralsky, include: (1) chloride; (2) bromide; and (3) sulphate.

(xv) *Chloropentaquo-salts*, $[Cr(H_2O)_5Cl]X_2$. These salts have been discussed in connection with the hydrates of chromic chlorides. They were discussed by N. Bjerrum, A. Recoura, R. F. Weinland and R. Krebs, and R. F. Weinland and T. Schumann. The series is represented by (1) chloride; (2) sulphate; and (3) chlorosulphate. J. Meyer and L. Speich made (4) the selenate.

(xvi) *Bromopentammines*, $[Cr(NH_3)_5Br]X_2$. These salts were studied by S. M. Jörgensen, and A. Werner and A. Miolati. They are represented by (1) chloride; (2) bromide, and (3) its bromoplatinate; (4) nitrate; and (5) chromate.

(xvii) *Bromoaquotetrammines*, $[Cr(NH_3)_4(H_2O)Br]X_2$. The salts were studied by P. T. Cleve, and P. Pfeiffer and S. Basci. They include: (1) chloride; (2) bromide; and (3) sulphate.

(xviii) *Bromoaquobisethylenediamines*, $[Cr\,en_2(H_2O)Br]X_2$. The salts were studied by P. Pfeiffer, P. Pfeiffer and R. Stern, and P. Pfeiffer and T. G. Lando. They include: (1) bromide; and (2) chromithiocyanate.

(xix) *Bromodiaquotriammines*, $[Cr(NH_3)_3(H_2O)_2Br]X_2$. A. Werner prepared (1) the chloride; (2) the bromide; and (3) the sulphate.

(xx) *Iodopentammines*, $[Cr(NH_3)_5I]X_2$. These salts were studied by A. Werner and A. Miolati, and S. M. Jörgensen. The salts include: (1) chloride, and (2) its chloroplatinate; (3) iodide; and (4) nitrate.

(xxi) *Iodoaquotetrammines*, $[Cr(NH_3)_4(H_2O)I]X_2$. P. T. Cleve prepared the iodide.

(xxii) *Thiocyanatopentammines*, $[Cr(NH_3)_5(SCy)]X_2$. The salts were studied by A. Werner and J. von Halban. The salts include: (1) chloride; (2) bromide; (3) nitrate; (4) thiocyanate; and (5) dichromate.

(xxiii) *Sulphatopentaquo-salts*, $[Cr(H_2O)_5(SO_4)]X_2$. The chloride was prepared by R. F. Weinland and T. Schumann.

III.—**The tetrammine family,** or compounds of the univalent basic group: $[CrA_4X'X']$. P. Larisch made some comparative observations on the solubilities of these salts.

(i) *Dihydroxydiaquodiammines*, $[Cr(NH_3)_2(H_2O)_2(OH)_2]X$. These salts were prepared by A. Werner and J. V. Dubsky, and A. Werner and J. L. Klein. The salts include: (1) chloride; (2) bromide; (3) iodide; (4) dithionate; and (5) thiocyanate.

(ii) *Dihydroxydiaquodipyridines*, $[Crpy_2(H_2O)_2(HO)_2]X$. These salts were prepared by P. Pfeiffer, P. Pfeiffer and W. Osann, and P. Pfeiffer and M. Tapuach. The salts include: (1) chloride; (2) bromide; (3) iodide; (4) sulphate; (5) nitrate; and (6) thiocyanate.

(iii) *Dichlorotetraquo-salts*, $[Cr(H_2O)_4Cl_2]X$, represented by J. Meyer and L. Speich's $[Cr(H_2O)_4Cl_2](SeO_4)_2[Cr(H_2O)_6]$. The salts are represented by the (1) chloride and its complexes with (2) antimonic chloride, and (3) cæsium chloride; as well as by the (4) sulphate. They were studied by A. Werner and A. Gubser, N. Bjerrum, R. F. Weinland and K. Feige, O. Stelling, and P. Pfeiffer.

(iv) *Dihydroxydiaquoethylenediamines*, $[Cr(H_2O)_2\,en(OH)_2]X$. These salts, prepared by E. Weinmann, include: (1) chloride; (2) perchlorate; (3) bromide; (4) iodide; (5) dithionate; and (6) thiocyanate.

(v) *Dichlorobisethylenediamines*, $[Cr\,en_2Cl_2]X$. These salts were studied by A. Werner, P. Pfeiffer, P. Pfeiffer and P. Koch, P. Pfeiffer and T. G. Lando, P. Pfeiffer and R. Stern, and P. Pfeiffer and A. Trieschmann. There are the isomeric forms:

(*a*) *Inactive salts*, including (1) chloride and (2) its antimonichloride, and (3) chloroplatinate; (4) bromide; (5) iodide; (6) sulphate; (7) dithionate; (8) nitrate; and (9) thiocyanate.

(*b*) *Dextro-cis salts*, including (1) chloride; (2) bromide, and (3) its bromocamphorsulphonate; and (4) nitrate.

(*c*) *Lævo-cis-salts*, including (1) chloride; (2) bromide, and (3) its bromocamphorsulphonate; and (4) nitrate.

(*d*) *Trans-salts*, including (1) chloride, and (2) its hydrochloride, and (3) chloroplatinate; (4) bromide; (5) iodide; (6) dithionate; (7) nitrate; (8) chromidioxalatoethylenediamine; and (9) thiocyanate.

(vi) *Dichloroaquotriammines*, $[Cr(NH_3)_3(H_2O)Cl_2]X$. These salts were prepared by A. Werner, F. Frowein, E. H. Riesenfeld and F. Seemann, and S. Guralsky, and include: (1) chloride; (2) iodide; (3) sulphate; (4) hydrosulphate; and (5) nitrate.

(vii) *Dibromoaquotriammines*, $[Cr(NH_3)_3(H_2O)Br_2]X$. These salts, prepared by S. Guralsky, include: (1) bromide; (2) iodide; (3) sulphate; (4) nitrate; and (5) thiocyanate.

(viii) *Dichlorodiaquodiammines*, $[Cr(NH_3)_2(H_2O)_2Cl_2]X$. A. Werner and J. L. Klein prepared the chloride.

(ix) *Dichlorodiaquodipyridines*, $[Crpy_2(H_2O)_2Cl_2]X$. These salts were prepared by P. Pfeiffer and M. Tapuach, and include: (1) chloride, and (2) its complex with pyridinium chloride; (3) bromide; and (4) nitrate.

(x) *Dibromotetraquo-salts*, $[Cr(H_2O)_4Br_2]X$. These salts are represented by the chloride prepared by N. Bjerrum.

(xi) *Dibromobisethylenediamines*, $[Cr\,en_2Br_2)X$. They were studied by P. Pfeiffer, and P. Pfeiffer and A. Trieschmann. There are isomeric forms:

(*a*) *Cis-salts*, including (1) bromide; (2) iodide; and (3) dithionate.

(*b*) *Trans-salts*, including (1) bromide and (2) its hydrobromide, and (3) its mercuribromide; (4) iodide; (5) dithionate; (6) nitrate; and (7) thiocyanate.

(xii) *Dichloroaquotriammines*, $[Cr(NH_3)_3(H_2O)Cl_2]X$. The chloride was studied by E. H. Riesenfeld and F. Seemann.

(xiii) *Dibromodiaquodiammines*, $[Cr(NH_3)_2(H_2O)_2Br_2]X$. A. Werner and J. L. Klein, and A. Werner and J. V. Dubsky studied the bromide.

(xiv) *Dibromodiaquopyridines*, $[Cr(NH_3)_2(H_2O)_2Br_2]X$. These salts were studied by A. Werner and A. Gubser, and P. Pfeiffer and M. Tapuach. The salts include: (1) bromide; (2) iodide; and (3) nitrate.

(xv) *Dibromotetraquo-salts*, $[Cr(H_2O)_4Br_2]X$. These salts were studied by A. Recoura, A. Werner and A. Gubser, A. Werner and R. Huber, P. Pfeiffer and M. Tapuach, and N. Bjerrum. The salts include: (1) chloride; (2) bromide; (3) sulphate; and (4) the cobaltic tetranitritodiammine.

(xvi) *Diiodobisethylenediamines*, $[Cr\,en_2I_2]X$. The double salt with mercuric iodide was studied by P. Pfeiffer and T. G. Lando.

(xvii) *Dithiocyanatotetrammines*, $[Cr(NH_3)_4(SCy)_2]X$. These salts were studied by P. Pfeiffer and M. Tilgner, and A. Werner and J. von Halban. The salts include: (1) chloride; (2) bromide; (3) sulphate; (4) nitrate; and (5) thiocyanate.

(xviii) *Dithiocyanatobisethylenediamines*, $[Cr\,en_2(SCy)_2]X$. These salts were studied by P. Pfeiffer and M. Haimann, P. Pfeiffer and P. Koch, P. Pfeiffer and R. Stern, and P. Pfeiffer. There are isomeric forms:

(*a*) *Cis-salts*, including (1) chloride; (2) bromide; (3) iodide and its complex with mercuric iodide; (4) sulphate; (5) nitrate; (6) thiocyanate; and (7) chromithiocyanate.

(*b*) *Trans-salts*, including (1) chloride; (2) bromide, (3) sulphate; (4) nitrate; (5) thiocyanate; and (6) chromithiocyanate.

(xix) *Oxalatotetrammines,* $[Cr(NH_3)_4(C_2O_4)]X$. These salts were studied by P. Pfeiffer and S. Basci. The salts include: (1) chloride; (2) bromide; (3) iodide; (4) nitrate; and (5) chromidioxalatodiammine.

(xx) *Oxalatobisethylenediamines,* $[Cr\,en_2(C_2O_4)]X$. These salts were studied by P. Pfeiffer, P. Pfeiffer and R. Stern, and P. Pfeiffer and A. Trieschmann, and H. Schwarz. The salts include: (1) bromide; (2) iodide; (3) chromidioxalatoethylenediamine; and (4) the chromidioxalatodiaquo-salt. Some other oxalato-salts were studied by R. Weinland and W. Hübner, and F. Hans.

IV.—**The triammine family,** or compounds of the null-valent group: $[CrA_3X_3']$.

(i) *Trichlorotriammine,* $[Cr(NH_3)_3Cl_3]$, was prepared by A. Werner, E. H. Riesenfeld and F. Seemann, F. Frowein, O. Stelling, S. Guralsky, and H. I. Schlesinger and co-workers. There are also the tribromide and the mixed chlorobromides.

(ii) *Trihydroxyaquodiammines,* $[Cr(NH_3)_2(H_2O)(OH)_3]$. The *tetrahydrate* was studied by A. Werner and J. L. Klein.

(iii) *Trihydroxyaquodipyridines,* $[Crpy_2(H_2O)(OH)_3]$. The *hexahydrate* was studied by P. Pfeiffer and M. Tapuach.

(iv) *Dichlorohydroxyaquodipyridine,* $[Crpy_2(H_2O)Cl_2]$. This salt was prepared by P. Pfeiffer and M. Tapuach.

(v) *Trichlorotripyridine,* $[Crpy_3Cl_3]$. This salt was examined by P. Pfeiffer. The addition products with (1) $2CH_3Cy$, and (2) C_2H_5Cy were examined by P. Pfeiffer.

(vi) *Trichloroaquodipyridine,* $[Crpy_2(H_2O)Cl_3]$. This salt was studied by P. Pfeiffer and M. Tapuach.

(vii) *Triaquotrichlorides,* $[Cr(H_2O)_3Cl_3]$. The addition product with 2Py.HCl was studied by P. Pfeiffer.

(viii) *Trisethylalcoholotrichloride,* $[Cr(C_2H_5.OH)_3Cl_3]$. This compound was examined by I. Koppel.

(ix) *Trichlorotrithiourea,* $[Cr(CSN_2H_4)_3Cl_3]$. *The hemihydrate* was examined by P. Pfeiffer.

(x) *Triaquotribromides,* $[Cr(H_2O)_3Br_3]$. The addition product with 2PyHBr was studied by P. Pfeiffer.

(xi) *Trithiocyanatotriammine,* $[Cr(NH_3)_3(SCy)_3]$. This compound was studied by A. Werner and J. von Halban.

(xii) *Trithiocyanatoaquodiammines,* $[Cr(NH_3)_2(H_2O)(SCy)_3]$. The monohydrate was studied by O. Nordenskjöld, J. A. Siemssen, and A. Werner and G. Richter; (1) the addition product with (2) ethylenediammine, (3) piperidine; (4) aniline, (5) brucine; and (6) pyridine were studied by O. Nordenskjöld, and J. A. Siemssen.

(xiii) *Dichlorothiocyanatotriammine,* $[Cr(NH_3)_3(SCy)Cl_2]$. This salt was prepared by S. Guralsky.

V.—**The diammine family,** or compounds of the univalent, acidic group: $[CrA_2X_4]$.

(i) *Tetrathiocyanatodiammines,* $[Cr(NH_3)_2(SCy)_4]M$. These compounds were studied by J. Morland, A. Reinecke, P. T. Cleve, O. Nordenskjöld, R. Escales and H. Ehrensperger, J. A. Siemssen, E. Orloff, O. T. Christensen, A. Werner and G. Richter, A. Werner and J. L. Klein, and P. Pfeiffer and M. Tilgner. The compounds include: (1) the acid and its monohydrate or dihyrate; (2) sodium; (3) potassium—*Reinecke's salt*—and (4) its complex with potassium iodide; (5) rubidium, and (6) a complex with pyridine; (7) cæsium, and (8) a complex with pyridine; (9) copper; (10) barium; (11) zinc, (12) a complex with pyridine; and (13) one with ammonia; (14) cadmium; (15) mercury; (16) iron; (17) cobalt; (18) ammonium and (19) its hydrate, and (20) iodide; (21) nitrosyl; (22) guanidine; (23) methylamine; (24) dimethylamine; (25) trimethylamine;

(26) ethylamine; (27) amylamine; (28) tetramethylammonium; (29) methylpyridinium; (30) methylquinolinium; (31) *m*-xylidinium; (32) ethylenediamine; (33) pentamethylenediamine; (34) aniline; (35) ammonium aniline; (36) *o*-toluidine; (37) *p*-toluidine; (38) phenylhydrazine; (39) piperidine; (40) pyridine; (41) picoline; (42) quinoline; (43) morphine; (44) quinine; (45) strychnine; (46) pilocarpine; and (47) cocaine.

(ii) *Tetrathiocyanatodipyridines*, $[CrPy_2(SCy)_4]M$. These compounds were studied by J. Sand and O. K. H. Burger, and P. Pfeiffer and W. Osann. The salts include: (1) potassium—the dihydrate, and tetrapyridine; (2) sodium—the trihydrate, and tetrapyridine; and (3) the mono- and di-pyridines.

(iii) *Tetrathiocyanatoethylenediamine*, $[Cr\,en(SCy)_4]M$. These compounds, prepared by E. Weinmann, include: (1) sodium; (2) potassium; (3) cæsium; (4) ammonium; (5) caffeine; (6) coniine; (7) nicotine; (8) narcotine; (9) codeïne; (10) strychnine; and (11) brucine.

(iv) *Dioxalatodiammines*, $[Cr(NH_3)_2(C_2O_4)_2]M$. P. T. Cleve, and P. Pfeiffer and S. Basci studied the complex which the group forms with chromic oxalatotetrammine.

(v) *Dioxalatoethylenediamines*, $[Cr\,en(C_2O_4)_2]M$. These salts were studied by H. Schwarz, P. Pfeiffer, P. Pfeiffer and A. Trieschmann, P. Pfeiffer and R. Stern, and P. Pfeiffer and R. Prade. The salts include: (1) potassium and its complex with potassium iodide; (2) the addition product with chromic *trans*-dichlorobisethylenediamine; (3) the addition product with chromic oxalatobisethylenediamine; (4) the addition product with cobaltic dichlorobisethylenediamine, and its dihydrate.

(vi) *Dioxalatodiaquo-salts*, $[Cr(H_2O)_2(C_2O_4)_2]M$. The (1) ammonium; (2) sodium; and (3) potassium salts were studied by A. Rosenheim and L. Cohn, and P. Pfeiffer and R. Stern.

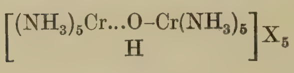
VI.—**The monammine family,** or compounds of the bivalent, acidic group: $[CrAX_5]$. These compounds are represented by the pentahalides—*vide supra*—studied by A. Werner, and A. Werner and A. Gubser—*e.g.*, (1) $M_2[Cr(H_2O)F_5]$; (2) $M_2[Cr(H_2O)Cl_5]$; and (3) $M_2[Cr(H_2O)Br_5]$.

VII.—**The hexa-acid family** or compounds of the tervalent, acidic group: $[CrX_6]$. These compounds are represented by (1) $M_3[CrF_6]$; (2) $M_3[CrCy_6]$; (3) $M_3[Cr(SCy)_6]$; and (4) $M_3[Cr(C_2O_4)_3]$, studied by H. Schwarz, L. A. Welo, P. Pfeiffer, and J. A. Siemssen.

B.—Polychromic compounds, that is, compounds with more than one chromium atom in the nucleus.

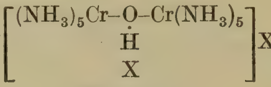
I.—**Dichromic salts**—with two chromium atoms in the nucleus. Some salts prepared by P. Schützenberger in 1868—*viz.* $[Cr_2O(CH_3COO)_3(NO_3)]$; $[Cr_2(CH_3COO)_4(NO_3)(OH)]$; and $[Cr_2(CH_3COO)_5.NO_3]$ may belong to this group. There are also salts of the type $[Cr_2(OH)(OOC.CH_2SCy)_4]X$, described by R. G. Krasnowskaja including the hydroxide, chloride, bromide, iodide, sulphate, and dithionate; and D. R. Camhi's $[Cr_2(OOC.CH_2Cy)_6OH]X$.

(i) *Hydroxydecammines*, $[Cr_2(OH)(NH_3)_{10}]X_5$. These salts were studied by S. M. Jörgensen, A. Werner, J. Petersen, and P. Pfeiffer. S. M. Jörgensen called them the *chromium rhodo-salts*; and A. Werner, *decammine-ol-dichromic salts*. The rhodo-salts include: (1) chloride, (2) its chloraurate, and (3) its chloroplatinate; (4) bromide, and (5) its bromoplatinate; (6) iodide; (7) sulphate; (8) dithionate; and (9) nitrate. These salts have a neutral reaction; and A. Werner represented them by the following formula in order to show their relationship with the isomeric erythro-salts—*vide infra*—which have an acidic reaction :



$$\left[(NH_3)_5Cr\ldots\underset{H}{O}-Cr(NH_3)_5\right]X_5$$

Rhodo-salts.



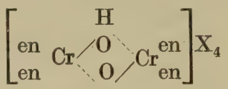
$$\left[(NH_3)_5Cr-\underset{\underset{X}{H}}{O}-Cr(NH_3)_5\right]X_4$$

Erythro-salts.

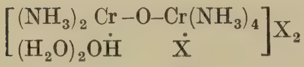
There are the so-called *basic rhodo-salts,* $[Cr_2(OH)(NH_3)_{10}]X_4(OH)$, studied by S. M. Jörgensen, and A. Werner. They are represented by (1) chloroiodide ; (2) bromide ; and (3) dithionate. The rhodo-salts are isomeric with the *erythro-salts* studied by S. M. Jörgensen, and represented by (1) chloroiodide ; (2) chloroplatinate ; (3) bromide ; (4) sulphate ; and (5) nitrate.

(ii) *Oxydecammines,* $[Cr_2O(NH_3)_{10}]X_4$, or $[(NH_3)_3Cr-O-Cr(NH_3)_5]X_4$. They were studied by S. M. Jörgensen, and A. Werner. The former called them *basic chromium erythro-salts.* They include : (1) bromide ; (2) dithionate ; and (3) nitrate.

(iii) *Dihydroxyaquatorethylenediamines,* $[Cr_2(OH)_2\,en_4]X_4$. They were studied by P. Pfeiffer and R. Stern. The salts include : (1) bromide ; and (2) iodide. P. Pfeiffer represented them by the formula :

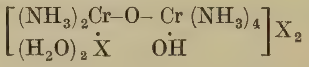


(iv) *Trihydroxyaquohexammines,* $[Cr_2(OH)_3(H_2O)(NH_3)_6]X_3$, or possibly $[Cr_4(OH)_6(NH_3)_{12}]X_6$. S. M. Jörgensen studied these salts and called them *chromium rhodoso-salts.* They were also studied by P. Pfeiffer, and J. Petersen. The salts include : (1) chloride, (2) its chloraurate, and (3) its chloroplatinate ; (4) bromide ; (5) iodide ; (6) polysulphide ; (7) sulphate ; (8) hydrosulphate ; (9) hydroxalate ; and (10) chromate. S. M. Jörgensen gave for the formula :



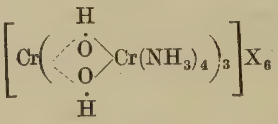
$$\left[\underset{(H_2O)_2OH}{(NH_3)_2\,Cr}-O-\underset{X}{Cr}(NH_3)_4\right]X_2$$

or



$$\left[\underset{(H_2O)_2X}{(NH_3)_2Cr}-O-\underset{OH}{Cr}\,(NH_3)_4\right]X_2$$

and P. Pfeiffer :



II.—**Trichromic salts** having three chromium atoms in the nucleus. Series of complex acetates, cyanoacetates, bromo-acetates, etc., were described by D. R. Camhi, J. A. Jwanowits, R. F. Weinland, G. Aschkinasy, and R. G. Krasnowskaja. In illustration, there are :

(i) *Hexacetatodihydroxytriammines,* $[Cr_3(CH_3COO)_6(OH)_2(NH_3)_3]X$, represented by the iodide prepared by R. F. Weinland and E. Büttner, and L. A. Welo.

(ii) *Hexacetatodihydroxytripyridines,* $[Cr_3Py_3(CH_3COO)_6(OH)_2]X$. These salts, prepared by R. F. Weinland and E. Gussmann, and L. A. Welo are represented by (1) hydroxystannichloride ; (2) chloroplatinate ; (3) iodide ; (4) nitrate ; (5) acetate ; (6) chloracetate ; (7) nitratacetate ; (8) ferricyanide ; (9) complex chromichromatodichromate ; and (10) permanganate.

(iii) *Chromic pentahydroxyaquodecammino-salts,* $[Cr_3(OH)_5(NH_3)_{10}(H_2O)](S_2O_3)_2.nH_2O$, and *chromic pentahydroxydiaquo-enneammino-salts, e.g.* $[Cr(OH)_5(NH_3)_9(H_2O)_2](S_2O_3)_2.3H_2O$ of P. Ray and P. B. Sarkar.

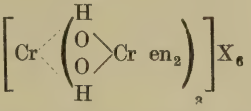
(iv) *Hexaformatodihydroxy-salts*, studied by L. A. Welo, R. Weinland and J. Lindner, etc.

(v) *Hexapropionatohydroxyfluoro-salts*, investigated by R. Weinland and J. Lindner.

III.—**Tetrachromic salts** having four chromium atoms in the nucleus.

(i) *Hexahydroxydodecammines—vide supra, trihydroxyaquohexammines.*

(ii) *Hexahydroxysexiesethylenediamines*, $[Cr_4(OH)_6\,en_6]X_6$. They were studied by P. Pfeiffer, and P. Pfeiffer and W. Vorster. The salts include: (1) chloride; (2) bromide; (3) iodide, and (4) its mercuri-iodide; (5) sulphate; (6) dithionate; (7) nitrate; (8) thiocyanate; and (9) chromate. P. Pfeiffer represented the constitution by the formula:



$$\left[Cr\left(\begin{matrix}H\\O\\O\\H\end{matrix}>Cr\ en_2\right)_3\right]X_6$$

About a dozen and a half salts, which have been reported, have not been fitted into A. Werner's system. When the salts are investigated more closely it may be possible to do something more with them. P. T. Cleve reported a *chromic tetramminosulphate*, $2Cr_2O_3.SO_3.4NH_3.24H_2O$; *chromic tetramminodinitrate*, $Cr_2O_3.N_2O_5.4NH_3.3H_2O$, *chromic diamminonitrate*, $2Cr_2O_3.N_2O_5.4NH_3.nH_2O$; and *ammonium chromic heptamminoctonitrate*, $2Cr(NO_3)_3.7NH_3.2NH_4NO_3.4\frac{1}{2}H_2O$; the *chromic diamminoxalate*, $Cr_2O_3.C_2O_3.2NH_3.8H_2O$, and *ammonium chromic hexamminotrioxalate*, $Cr_2(C_2O_4)_3.6NH_3.(NH_4)HCr_2O_4.1\frac{1}{2}H_2O$; and the *chromic heptamminonitratooxalate*, $2Cr(NO_3)(C_2O_4).7NH_3.3H_2O$; W. R. Lang and E. H. Jolliffe, *chromic quinquiesmethylaminotrichloride*, $CrCl_3.5CH_3NH_2$; W. R. Lang and C. M. Carson, *chromic quinquiesethylaminotrichloride*, $CrCl_3.5C_2H_5NH_2.H_2O$, and *chromic quaterethylamine*, $CrCl_3.4C_2H_5NH_2.H_2O$; and *chromic quaterethylenediaminotrichloride*, $CrCl_3.4C_2H_4(NH_2)_2H_2O$; O. Nordensjöld, *mercuric chromic sulphotrithiocyanatodiammine*, $Cr(SCy)_3(NH_3)_2.6HgS$; J. Sand and O. K. H. Burger, *chromic oxytetrathiocyanatotetrammine*, $Cr_2O(SCy)_4(NH_3)_4$; and *chromic oxytetrathiocyanatotetrapyridine*, $Cr_2O(SCy)_4Py_4$; E. A. Werner, *oxalatotriamminochromic acid*, $HCr(C_2O_4)_2(NH_3)_3.3H_2O$; *potassium oxalatotriamminochromate*, $KCr(C_2O_4)_2(NH_3)_3.3H_2O$; and *ammonium oxalatotriamminochromate*, $(NH_4)_5Cr_4(C_2O_4)_5(NH_3)_3.14H_2O$.

REFERENCES.

[1] G. Aschkinasy, *Ueber komplexe Chromacetate*, Zürich, 1910; A. Werner and G. Aschkinasy, *Ber.*, **41**. 3458, 1908; G. A. Barbieri, *Atti Accad. Lincei*, (5), **22**. 867, 1913; (5), **24**. 916, 1915; A. Benrath, *Zeit. anorg. Chem.*, **177**. 286, 1928; A. G. Berghman, *Journ. Russ. Phys. Chem. Soc.*, **56**. 177, 1925; N. Bjerrum, *Zeit. phys. Chem.*, **59**. 581, 1907; *Ber.*, **40**. 2917, 1907; D. R. Camhi, *Ueber complexe Chromsalze*, Zürich, 1911; I. I. Chernyeff, *Ann. Inst. Plat. Leningrad*, 5, 1927; O. T. Christensen, *Journ. prakt. Chem.*, (2), **23**. 27, 1881; (2), **24**. 75, 1881; (2), **45**. 213, 356, 1881; P. T. Cleve, *Oefvers. Akad. Förh.*, 165, 1861; *Svenska Akad. Hand.*, **6**. 4, 1865; *Lärobok i oorganisk Kemi*, Stockholm, 307, 1873; 354, 1877; J. V. Dubsky, *Journ. prakt. Chem.*, (2), **90**. 61, 1914; F. Ephraim and W. Ritter, *Helvetica Chim. Acta*, **11**. 848, 1928; R. Escales and H. Ehrensperger, *Ber.*, **36**. 2681, 1903; E. Frémy, *Compt. Rend.*, **47**. 886, 1858; G. Florence and E. Couture, *Bull. Soc. Chim.*, (4), **39**. 643, 1926; F. Frowein, *Zeit. anorg. Chem.*, **110**. 107, 1920; S. Guralsky, *Ueber Di- und Triamminchromisalze*, Zürich, 1909; F. Hans, *Ueber Chromi-oxalsäure-halogen (rhodan)-Verbindungen*, Würzburg, 1924; O. Hassel and G. B. Næss, *Zeit. anorg. Chem.*, **174**. 24, 1928; C. Hertwig, *Liebig's Ann.*, **45**. 298, 1843; A. Hiendlmayr, *Beiträge zur Chemie der Chrom- und Kobalt-Ammoniake*, Freising, 1907; F. M. Jäger, *Zeit. Kryst.*, **39**. 541, 1904; S. M. Jörgensen, *Journ. prakt. Chem.*, (2), **20**. 105, 1879; (2), **25**. 88, 322, 402, 1882; (2), **29**. 413, 1884; (2), **30**. 1, 1884; (2), **42**. 206, 1890; (2), **44**. 66, 1891; (2), **45**. 260, 274, 1892; *Zeit. anorg. Chem.*, **16**. 195, 1898; M. Kilpatrick, *Journ. Amer. Chem. Soc.*, **50**. 358, 1928; J. A. Jwanowits, *Das Chrom in komplexen Ionen*, Zürich, 1911; A. Werner and J. A. Jwanowits, *Ber.*, **41**. 5462, 1908; R. F. Weinland and J. A. Jwanowits, *ib.*, **41**. 3233, 1908; H. J. S. King, *Journ. Chem. Soc.*, **125**. 1329, 1924; **127**. 2100, 1925; I. Koppel, *ib.*, **28**. 461, 1901; R. G. Krasnowskaja, *Ueber komplex Chromverbindungen mit Brom- und Rhodanessigsäure*, Zürich, 1912; W. R. Lang and C. M. Carson, *Journ. Amer. Chem. Soc.*, **26**. 414, 758, 1904; W. R. Lang and E. H. Jolliffe, *ib.*, **26**. 417, 1904; P. Larisch, *Ueber die Abhängigkeit der Löslichkeit von der Anzahl der Ionen bei den Kobalt-, Chrom-, Rhodium-, Iridium-, und Platin-Ammoniaken*, Zürich, 1904; J. Meyer and L. Speich, *Zeit. anorg. Chem.*, **118**. 1, 1921; J. Morland, *Journ. Chem. Soc.*, **13**. 252, 1861; O. Nordenskjöld, *Zeit. anorg. Chem.*, **1**. 132, 1892; E. Orloff, *Journ. Chim. Ukraine*, **1**. 378, 1925; J. Petersen, *Zeit. phys. Chem.*, **10**. 580, 1892; P. Pfeiffer, *Zeit. anorg. Chem.*, **24**. 279, 1900; **29**. 107, 1901; **31**. 401 1902; **36**. 349, 1903; **55**. 97, 1907; **56**. 261, 279, 1907; **58**. 228, 272, 292,

317, 1908 ; in L. Gmelin and K. Kraut, *Handbuch der anorganischen Chemie,* Heidelberg, **3.** i, 489, 1912 ; *Liebig's Ann.*, **342.** 283, 1906 ; **346.** 28, 1906 ; *Ber.*, **33.** 2686, 1900 ; **34.** 2559, 4303, 1901 ; **36.** 1926, 1903 ; **37.** 4255, 1904 ; **39.** 1864, 1906 ; **40.** 3126, 3828, 4026, 4036, 1907 ; P. Pfeiffer and S. Basci, *ib.*, **38.** 3594, 1905 ; *Liebig's Ann.*, **346.** 46, 1906 ; S. Basci, *Beitrag zur Chemie ammoniakalischer Chromsalze,* Zürich, 1907 ; P. Pfeiffer and T. Gassmann, *Liebig's Ann.*, **346.** 59, 1906 ; *Zeit. anorg. Chem.*, **58.** 301, 1908 ; M. Haimann, *Ueber Coordinationsisomerie bei Chromiaken,* Zürich, 1912 ; P. Pfeiffer and M. Haimann, *Liebig's Ann.*, **346.** 72, 1906 ; *Ber.*, **36.** 1063, 1903 ; P. Koch, *Beiträge zur Stereoisomerie der Chromsalze,* Zürich, 1905 ; P. Pfeiffer and P. Koch, *Ber.*, **37.** 4268, 4282, 1904 ; *Zeit. anorg. Chem.*, **56.** 293, 1907 ; P. Pfeiffer and T. G. Lando, *ib.*, **56.** 292, 1907 ; *Ber.*, **37.** 4275, 1904 ; T. G. Lando, *Beitrag zur Kenntnis der Aquo- und Diacido-diaethylendiaminchromsalze,* Zürich, 1904 ; W. Osann, *Zur Chemie der Dipyridinchromsalze,* Zürich, 1907 ; P. Pfeiffer and W. Osann, *Ber.*, **39.** 1873, 2121, 1906 ; **40.** 4031, 1907 ; P. Pfeiffer and H. Pietsch, *Zeit. anorg. Chem.*, **58.** 297, 1908 ; P. Pfeiffer and R. Prade, *ib.*, **58.** 249, 1908 ; P. Pfeiffer and R. Stern, *ib.*, **58.** 240, 280, 1908 ; *Ber.*, **40.** 2832, 1907 ; J. N. Brönsted and A. Petersen, *Journ. Amer. Chem. Soc.*, **43.** 2265, 1921 ; R. Stern, *Beitrag zur Chemie der Aquochromsalze,* Zürich, 1908 ; M. Tapuach, *Zur Kenntnis der Hydratisomerie bei Di- und Trihalogenochromsalzen,* Zürich, 1907 ; P. Pfeiffer and M. Tapuach, *Ber.*, **39.** 1874, 1879, 1906 ; **40.** 4043, 1907 ; *Zeit. anorg. Chem.*, **49.** 437, 1906 ; P. Pfeiffer and M. Tilgner, *ib.*, **55.** 366, 1907 ; **58.** 439, 1908 ; P. Pfeiffer and A. Trieschmann, *ib.*, **56.** 283, 1907 ; *Liebig's Ann.*, **342.** 283, 1906 ; *Ber.*, **37.** 4287, 1904 ; **40.** 3837, 1907 ; A. Trieschmann, *Beitrag zur Stereoisomerie und Koordinationsisomerie bei Chromsalzen,* Zürich, 1906 ; P. Pfeiffer and W. Vorster, *Zeit. anorg. Chem.*, **58.** 286, 1908 ; F. Pintus, *Ueber die Existenz des einwertigen Chroms und den Einfluss der Komplexkonstitution auf die Bildung chromorganischer Verbindungen,* Leipzig, 1928 ; P. Ray and P. B. Sarkar, *Journ. Indian Chem. Soc.*, **1.** 91, 1924 ; A. Recoura, *Bull. Soc. Chim.*, (3), **27.** 1156, 1902 ; P. Schützenberger, *Compt. Rend.*, **66.** 814, 1868 ; A. Reinecke, *Liebig's Ann.*, **126.** 113, 1863 ; E. H. Riesenfeld and F. Seemann, *Ber.*, **42.** 4231, 1909 ; F. Seemann, *Ueber Chromiaquo-Triammine,* Freiburg, 1910 ; A. Rosenheim and L. Cohn, *Zeit. anorg. Chem.*, **28.** 337, 1901 ; L. Cohn, *Ueber den direkten Ersatz von Ammoniak in Metallammoniaken durch Säurereste,* Zürich, 1906 ; J. Sand and O. K. H. Burger, *Ber.*, **39.** 1772, 1906 ; H. I. Schlesinger and R. K. Worner, *Journ. Amer. Chem. Soc.*, **51.** 3520, 1929 ; H. I. Schlesinger and D. N. Rickles, *ib.*, **51.** 3523, 1929 ; H. Schwarz, *Ueber die Beziehungen zwischen Metallammoniaken und komplexen Salzen,* Zürich, 1903 ; W. J. Sell, *Proc. Roy. Soc.*, **33.** 267, 1882 ; **45.** 321, 1889 ; J. A. Siemssen, *Ueber komplexe Verbindungen mit NH_3- oder amminhaltigen negativen Radikalen,* Zürich, 1909 ; O. Stelling, *Zeit. Elektrochem.*, **34.** 520, 1928 ; M. Siewert, *Zeit. ges. Naturwiss.*, **18.** 244, 1861 ; C. W. Vincent, *Phil. Mag.*, (4), **13.** 191, 1857 ; R. F. Weinland, *Ber.*, **41.** 3237, 1908 ; **42.** 3828, 1909 ; R. F. Weinland and E. Büttner, *Zeit. anorg. Chem.*, **67.** 171, 1910 ; E. Büttner, *Ueber grüne und violette komplexe Chromiacetate,* Tübingen, 1918 ; R. F. Weinland and K. Feige, *Ber.*, **36.** 244, 1903 ; R. F. Weinland and E. Gussmann, *Ber.*, **42.** 3881, 1909 ; *Zeit. anorg. Chem.*, **67.** 167, 1910 ; R. Krebs, *Ueber Chromchloridsulfate und Chromsulfate,* Tübingen, 1906 ; R. F. Weinland and R. Krebs, *Zeit. anorg. Chem.*, **48.** 251, 1906 ; **49.** 160, 1906 ; R. F. Weinland and T. Schumann, *ib.*, **58.** 176, 1908 ; *Ber.*, **40.** 3091, 1907 ; R. Weinland and W. Hübner, *Zeit. anorg. Chem.*, **178.** 275, 1929 ; R. Weinland and J. Lindner, *ib.*, **190.** 285, 1930 ; E. Weinmann, *Diammidoverbindungen mit besonderer Rücksichtnahme auf die Tetrarhodanatodiamido-chromi-Salze,* Zürich, 1919 ; A. Werner, *Neue Anschauungen auf dem Gebiete der anorganische Chemie,* Braunschweig, 290, 1908 ; London, 1911 ; *Zeit. anorg. Chem.*, **3.** 293, 1893 ; *Ber.*, **39.** 2663, 1906 ; **43.** 2290, 1910 ; **44.** 3132, 1911 ; A. Werner and J. V. Dubsky, *ib.*, **40.** 4089, 1907 ; J. V. Dubsky, *Ueber basische Salze, deren Zusammensetzung und Beziehungen,* Zürich, 1908 ; A. Werner and A. Gubser, *Ber.*, **34.** 1579, 1901 ; **39.** 1823, 1906 ; *Liebig's Ann.*, **322.** 337, 1902 ; A. Gubser, *Ueber die Hydrate des Chromchloride,* Zürich, 1900 ; J. von Halban, *Untersuchungen über Chromammoniakverbindungen,* Zürich, 1902 ; L. A. Welo, *Phil. Mag.*, (7), **6.** 481, 1928 ; A. Werner and J. von Halban, *Ber.*, **39.** 2669, 1906 ; A. Werner and R. Huber, *ib.*, **39.** 336, 1906 ; A. Werner and D. Kalkmann, *Liebig's Ann.*, **322.** 296, 1902 ; A. Werner and J. L. Klein, *ib.*, **35.** 283, 1902 ; J. L. Klein, *Ueber Tetraquodiammin- und Diacidodiaquo-diamminchromsalze,* Zürich, 1902 ; A. Werner and A. Miolati, *Zeit. phys. Chem.*, **14.** 508, 1894 ; A. Werner and G. Richter, *Zeit. anorg. Chem.*, **15.** 261, 1897 ; E. A. Werner, *Journ. Chem. Soc.*, **53.** 409, 1888 ; **85.** 1438, 1904 ; E. Wilke-Dörfurt and G. Balz, *Zeit. anorg. Chem.*, **159.** 197, 1927 ; E. Wilke-Dörfurt, G. Balz and A. Weinhardt, *ib.*, **185.** 417, 1930 ; E. Wilke-Dörfurt and K. Niederer, *ib.*, **184.** 145, 1929 ; E. Wilke-Dörfurt and H. G. Mureck, *ib.*, **184.** 121, 1930 ; E. Wilke-Dörfurt and R. Pfau, *Zeit. Elektrochem.*, **36.** 118, 1930 ; E. Wilke-Dörfurt and A. Weinhardt, *Zeit. anorg. Chem.*, **184.** 147, 1929.

§ 25. The Complex Salts of Chromic Chloride

S. M. Jörgensen[1] treated mercuric chromic hexamminochloride—made by adding mercuric chloride to a hydrochloric acid soln. of chromic hexamminonitrate—with hydrogen sulphide, and obtained a liquid from which yellow crystals of **chromic hexamminotrichloride,** $[Cr(NH_3)_6]Cl_3.H_2O$, were obtained. The salt is freely soluble in water ; and when treated with hydrochloric acid, it forms the chloropentamminodichloride, $[Cr(NH_3)_5Cl]Cl_2$. W. Biltz and E. Birk gave 1·585 for the sp. gr. of the hexammine at 25°/4° and 175·8 for the mol. vol. Y. Shibata measured the absorption spectrum. S. Aoyama and co-workers studied the X-ray absorption and constitution. A. Werner and A. Miolati found that a mol of the salt in v-litres of water at 25° had the mol. conductivity μ ;

v . .	125	250	500	1000	2000
μ . .	353·5	388·6	418·8	441·7	463·6 mhos.

E. Birk studied the mol. vol. of the ammonia in the ammines. H. J. S. King calculated 180·0 for the ionic mobility at 0° and 370·2 at 25°. F. Ephraim and P. Mosimann discussed the solubilities of the hexammines; O. Stelling, the X-ray spectrum; and H. Lessheim and co-workers, the electronic structure. A. Benrath found that in the presence of hydrochloric acid the stable phase is $[Cr(NH_3)_5Cl]Cl_2$. P. Pfeiffer also prepared *chromic trisethylenediaminotrichloride,* $[Cr\,en_3]Cl_3,3\frac{1}{2}H_2O$. O. T. Christensen obtained **chromic aquopentamminotrichloride,** $[Cr(H_2O)(NH_3)_5]Cl_3$, from a soln. of the base in hydrochloric acid. S. M. Jörgensen also prepared this salt. The orange-yellow crystals are freely soluble in water. The dil. aq. soln. is decomposed when boiled, but the acidified soln. is more stable. When boiled with hydrochloric acid, the chloropentamminochloride is formed. All three chlorine atoms are immediately precipitated by the addition of silver nitrate. F. Ephraim and W. Ritter obtained the salt by the action of an ammoniacal soln. of ammonium nitrate on potassium or ammonium chromic chloride. H. J. S. King also prepared this salt; and he gave for the conductivity, μ mhos, of a mol. of the salt in v litres at 0° :

v . .	32	64	128	256	512	1024
μ . .	169·5	186·3	197·6	218·4	232·9	247·8

For the mol. conductivity, μ, of soln. of a mol of the salt in v litres of water at 25°, A. Werner and A. Miolati gave :

v . .	125	250	500	1000	2000
μ . .	221·0	239·3	252·0	261·0	271·6

Values were also obtained by H. J. S. King who gave 174·3 for the ionic mobility at 0° of the $[Cr(NH_3)_5(H_2O)]^{\cdots}$-ion. F. Ephraim and W. Ritter found that the salt absorbs ammonia at a low temp., and the decomposition curve shows breaks corresponding with a tetrammine, and doubtful breaks for the hexammine and diammine. A. Benrath found that the stable phase in the presence of hydrochloric acid is $[Cr(NH_3)_5Cl]Cl_2$. P. Pfeiffer prepared **chromic diaquotetramminotrichloride,** $[Cr(H_2O)_2(NH_3)_4]Cl_3$, from a hydrochloric acid soln. of chromic hydroxyaquotetramminodithionate. The brick-red crystalline powder is soluble in water. The conc. aq. soln. gives an orange-red precipitate with potassium cobalticyanide and a brick-red precipitate with conc. hydrochloric or hydrobromic acid. Silver nitrate precipitates all three chlorine atoms. The salt gradually passed into the aquochlorotetramminodichloride. E. H. Riesenfeld and F. Seemann, and F. Frowein prepared **chromic triaquotriamminotrichloride,** $[Cr(NH_3)_3(H_2O)_3]Cl_3$, by dissolving chromic tetroxytriammine in dil. hydrochloric acid and passing hydrogen chloride into the resulting soln. After a time, bright red, needle-shaped crystals of the triaquotriamminotrichloride separate. If the hydrogen chloride is passed in for too long a time, the soln. becomes green in colour, and crystals of either the dichromic or the grey dichloroaquotriamminochloride, are obtained. A. Werner obtained the salt by dissolving chromium triamminotetroxide in hydrochloric acid (1 : 4) and saturating the cold soln. with hydrogen chloride; he also obtained it by covering a mixture of a gram of dichloroaquotriamminochloride and 8 c.c. of water with 5 c.c. of pyridine, and adding solid potassium iodide; the resulting chromium triamminotriaquohydroxyiodide is treated with conc. hydrochloric acid, and the resulting triamminotriaquotrichloride is purified by passing hydrogen chloride through the aq. soln. F. Frowein found that the dichloroaquotriamminochloride in aq. soln. gradually changes into the chlorodiaquotriamminodichloride ; and this, in turn, into the triaquotriamminotrichloride. The changes can be followed by the change of colour of the soln., that of the monoaquo-salt being blue, that of the diaquo-salt reddish-violet, and that of the triaquo-salt red. These changes are more rapid the more dil. the soln. The conductivity of the monoaquo-compound is lowest, that of the triaquo-compound highest, so that the change is accompanied by a gradual increase in conductivity of the soln. No direct transformation of the mono- into the tri-aquo-salt occurs, but the diaquo-salt is always the first hydration product of the monoaquo-compound. The measurements agree with the hypothesis that the compounds contain no water outside the inner sphere, that is, they are purely co-ordinated compounds. The soln. of the triaquo-compound undergoes slow decomposition, the conductivity curve first showing a maximum, followed by a minimum. Deposition of chromium hydroxide eventually takes place, but intermediate complex compounds are probably first formed. A. Werner also prepared **chromium triamminotriaquodichloronitrate,** $[Cr(H_2O)_3(NH_3)_3]Cl_2(NO_3)$, and also **chromium triamminotriaquotriperchlorate,** $[Cr(H_2O)_3(NH_3)_3](ClO_4)_3$.

P. Pfeiffer and R. Stern prepared **chromic cis-diaquobisethylenediaminotrichloride,** $[Cr\ en_2(H_2O)_2]Cl_3.2H_2O$, and P. Pfeiffer and R. Prade obtained the **trans-salt ;** A. Werner and J. L. Klein obtained **chromic tetraquodiamminotrichloride,** $[Cr(H_2O)_4(NH_3)_2]Cl_3$, from a hydrochloric acid soln. of the bromide. The pale red, monoclinic prisms are freely soluble in water, and insoluble in alcohol. P. Pfeiffer, and P. Pfeiffer and M. Tapuach prepared **chromic tetraquodipyridinotribromide,** $[CrPy_2(H_2O)_4]Br_3.2H_2O$. The preparation of **chromic hexaquotrichloride,** $[Cr(H_2O)_6]Cl_3$, by N. Bjerrum, A. Werner and A. Gubser, A. Werner and R. Huber, A. Weinland and R. Krebs, R. F. Weinland and T. Schumann, and P. Pfeiffer has been previously described.

H. J. S. King prepared rose-red needles of **chromic hydroxypentamminochloride,** $[Cr(NH_3)_5(OH)]Cl_2.H_2O$, by dissolving the aquopentamminochloride in conc. ammonia, and precipitating with alcohol. He gave for the conductivity, μ mho, of a mol of the salt in v litres at 0° and 25° :

v . .	32	64	128	256	512	1024
0° . .	108·8	119·0	127·5	134·9	138·8	147·2
25° . .	206·2	225·7	239·0	253·0	261·9	274·6

He calculated 73·3 for the ionic mobility at 0° and 131·8 at 25°. P. Pfeiffer and R. Stern prepared **chromic cis-hydroxyaquobisethylenediaminodichloride,** $[Cr\ en_2(H_2O)(OH)]Cl_2.H_2O$; P. Pfeiffer, **chromic hydroxydiaquodipyridinodichloride,** $[CrPy_2(H_2O)_2(OH)]Cl_2$; and O. T. Christensen, **chromic nitritopentamminodichloride,** $[Cr(NH_3)_5(NO_2)]Cl_2$, by the action of dil. nitric acid on the chloride of the series. A. Werner and A. Miolati found the electrical conductivity of soln. with a mol of the salt in 125, 250, 500, 1000, and 2000 litres of water at 25° to be respectively μ=221·0, 239·3, 252·0, 261·0, and 271·6.

S. M. Jörgensen prepared **chromic chloropentamminodichloride,** $[Cr(NH_3)_5Cl]Cl_2$, by reducing, say, 25 grms. of violet chromic chloride with hydrogen at a red-heat, and treating the product with a soln. of ammonium chloride in conc. aq. ammonia. Air is then passed through the blue liquid until oxidation is complete. Two litres of hydrochloric acid are added and the mixture is boiled for a few minutes when the salt separates as a carmine-red powder. This is washed with a mixture of hydrochloric acid (1 : 1), dissolved in dil. sulphuric acid, and filtered into a great excess of cold, conc. hydrochloric acid. The precipitate is boiled with hydrochloric acid, washed first with cold acid and water, then with alcohol, and finally dried in air at ordinary temp. F. Ephraim and W. Ritter obtained the salt by the action on potassium or ammonium chromic chloride of an ammoniacal soln. of ammonium nitrate. O. T. Christensen obtained it by reducing a soln. of potassium dichromate with alcohol and hydrochloric acid, and treated the clear liquid in the absence of air with conc. hydrochloric acid and zinc. The blue liquid was then digested with ammonium chloride and conc. ammonia, and air passed through the liquor. The soln. was then boiled a short time with conc. hydrochloric acid. O. T. Christensen, and W. R. Lang and C. M. Carson also made the same salt by digesting violet chromic chloride with liquid ammonia. A. Werner and J. von Halban, S. M. Jörgensen, and O. T. Christensen also prepared this salt by the action of hydrochloric acid on some of the other chromic ammines. S. M. Jörgensen described the salt as a red crystalline powder consisting of octahedra of sp. gr. 1·687. R. Klement gave 1·696 for the sp. gr. and 143·7 for the mol. vol. Y. Shibata measured the absorption spectrum. A. Werner and A. Miolati found that a mol of the salt in v litres of water at 25° has the mol. conductivity, μ :

v	125	250	500	1000	2000
μ	221·7	239·0	250·5	260·2	269·9

H. J. S. King gave for the conductivity, μ mhos, of a mol of the salt in v litres :

	v	64	128	256	512	1024
μ	0°	123·1	131·1	137·2	142·3	147·6
	25°	230·3	244·5	255·0	264·4	276·8

The ionic mobility at 0° is 75·2 and at 25°, 139·7. E. Rosenbohm found the magnetic susceptibility to be $25{\cdot}76\times10^{-6}$ mass units ; and L. A. Welo gave $24{\cdot}80\times10^{-6}$. A. Benrath found that the salt is stable in the presence of hydrochloric acid. S. M. Jörgensen found that 100 grms. of water at 16° dissolve 0·65 grm. of the salt forming a violet-red soln. which, when exposed to light, deposits hydrated chromic oxide. When the soln. is kept in the dark, or boiled, it passes into the aquochlorotetramminodichloride. When the aq. soln. is boiled it forms the aquopentamminochloride ; boiling soda-lye precipitates chromic hydroxide. The rate of hydrolysis of the salt was investigated by A. Werner and A. Miolati, A. B. Lamb and J. W. Marden, H. Freundlich and H. Pape, and H. Freundlich and R. Bartels. S. M. Jörgensen added that the aquochlorotetramminodichloride gives the following reactions : With sodium hypochlorite, nitrogen is evolved, and the chromium is oxidized to chromic acid. Its soln. gives a precipitate with conc. hydrochloric acid, owing to the insolubility of the chloride in acid. With hydrobromic acid, it gives a crystalline precipitate of the bromide, and with solid potassium iodide one of the iodide. When boiled with potassium cyanide, it turns yellow. Conc. nitric acid precipitates the chloro-nitrate. Hydrosilicofluoric acid throws down the red crystalline chlorofluosilicate. Platinic chloride precipitates, even from a very dil. soln., the chloropurpureochromium platinochloride. Sodium bromoplatinate gives an analogous precipitate. Mercuric chloride gives red needles of the double salt. Precipitates are also produced by potassium mercuric bromide and iodide, by sodium dithionate, potassium chromate, and dichromate, ammonium molybdate, and phosphomolybdate, and by picric and oxalic acids. In these respects this salt closely resembles the analogous cobalt salt. On treatment with silver nitrate only two atoms of chlorine are removed, and the chloro-nitrate is formed. By rubbing the solid chloride with silver oxide and water the aquochlorotetramminodichloride is formed. S. M. Jörgensen also prepared the sulphide, sulphate, hydrosulphate, dithionate, fluosilicate, nitrate, bromide, iodide, oxalate, ferrocyanide, and chromate, as well as complex mercury and platinic halides of the chromic chloropentammines. F. Ephraim and W. Ritter found that the chloropentamminodichloride does not absorb ammonia gas.

In 1858, E. Frémy obtained a salt which P. T. Cleve showed to be **chromic chloroaquotetramminodichloride,** $[Cr(NH_3)_4(H_2O)Cl]Cl_2$. It was prepared by allowing a sat. soln. of chromium chloride in aq. ammonia to stand in a closed vessel until the liquid acquired a red colour; it was then exposed to the air when it deposited a dark reddish-violet powder. The soln. of the salt in hydrochloric acid, when treated with an excess of conc. hydrochloric acid, furnished rose-red crystals of the aquochlorotetramminodichloride. S. M. Jörgensen obtained the salt by heating a conc. aq. soln. of 100 grms. of ammonium dichromate with 300 c.c. of hydrochloric acid of sp. gr. 1·17, 200 grms. of ammonium chloride, and 60–70 c.c. of alcohol, and evaporating to dryness. The product was digested for 24 hours with a litre of conc. ammonia; the residue was dissolved in hydrochloric acid, and treated anew with ammonia. The ammoniacal soln. was mixed with 4 litres of conc. hydrochloric acid; the precipitate was freed from ammonium chloride by hydrochloric acid (1 : 1). The mixture was dissolved in water and treated with a soln. of ammonium sulphate (1 : 5), and the precipitate washed with cold water; and digested with hydrochloric acid (1 : 1). S. M. Jörgensen also obtained the salt as a by-product in preparing the oxalatotetramminonitrate. P. Pfeiffer and S. Basci agitated 100 grms. of green hexahydrated chromic chloride with 155 c.c. of pyridine; and after adding 600 c.c. of water, allowed the mixture to stand for 7 to 10 hrs. Ten grams of the diaquodipyridinochloride were digested with 56 c.c. of 25 per cent. aq. ammonia at 45° to 48°. The deep reddish-violet soln. was treated with 68 c.c. of hydrochloric acid of sp. gr. 1·19. After standing 4 or 5 hrs. at ordinary temp., the prismatic crystals were separated from the mother-liquor. P. Pfeiffer obtained the same salt from the diaquotetramminochloride and hydrochloric acid. The deep red rhombic crystals are stable in air, but not if exposed to light. J. Peterson obtained a mol. wt. 262 by the f.p. method when the theoretical value is 251·5. Y. Shibata measured the absorption spectrum. A. Werner and A. Miolati found that a mol of the salt in v litres of water had the mol. conductivity, μ, at 25°,

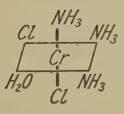
v . .	125	250	500	1000	2000
μ . .	212·6	231·6	245·6	261·2	274·8

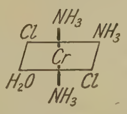
S. M. Jörgensen found that 100 grms. of water at 15° dissolve 6·4 grms. of the salt. The salt is decomposed when the soln. in water or alkali-lye is boiled; hydrochloric acid precipitates the salt from the aq. soln. Oxalic acid precipitates from the soln., after standing some weeks, $Cr_2(C_2O_4)_3.6NH_3.3H_2O$; ammonium oxalate precipitates from the warm soln. chromic oxalate tetramminochloride and with potassium thiocyanate, P. Pfeiffer and M. Tilgner obtained chromic dithiocyanatotetramminothiocyanate; with pyridine and sodium dithionate, P. Pfeiffer obtained chromic hydroxyaquotetramminodithionate. P. T. Cleve found that conc. sulphuric acid expels only two-thirds of the chlorine as hydrochloric acid; and S. M. Jörgensen, that a nitric acid soln. of silver nitrate precipitates only two-thirds of the chlorine as silver chloride. There are also the sulphate, sulphide, nitrate, fluosilicate, bromide, iodide, oxalate, and chromate as well as complexes of the chloride with the mercuric and platinic chlorides of the aquochlorotetrammines. N. Bjerrum, R. F. Weinland and R. Krebs, R. F. Weinland and T. Schumann, and A. Recoura described **chromic chloropentaquodichloride,** $[Cr(H_2O)_5Cl]Cl_2$—*vide supra.* H. J. S. King found the conductivity, μ mhos, of a mol of the salt in v litres, to be:

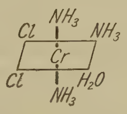
	v . .	64	128	256	512	1024
μ	0° . .	—	134·8	142·1	146·8	151·2
	25° . .	232·3	247·7	261·5	272·9	280·6

B. Klement gave 1·961 for the sp. gr., and 143·7 for the mol. vol. A. Werner and A. Miolati found that a soln. of a mol of the salt in 125, 250, 500, 1000, and 2000 litres of water at 25° had the mol. conductivity μ=235·7, 257·5, 270·6, 280·1, and 283·6 respectively. P. T. Cleve prepared **chromic bromoaquotetramminodichloride,** $[Cr(NH_3)_4(H_2O)Br]Cl_2$, by the action of fuming hydrochloric acid on the bromide. S. M. Jörgensen prepared **chromic iodopentamminodichloride,** $[Cr(NH_3)_5I]Cl_2$, by the action of hydrochloric acid on the iodide. A. Werner and A. Miolati found that a mol of the salt in 125, 250, 500, 1000, and 2000 litres of water at 25° had the mol. conductivity $\mu=273{\cdot}8$, $292{\cdot}5$, $312{\cdot}1$, $326{\cdot}9$, and $342{\cdot}8$ respectively. The chloroplatinate was also obtained. F. Frowein, and E. H. Riesenfeld and F. Seeman prepared **chromic chlorodiaquotriamminodichloride,** $[Cr(NH_3)_3(H_2O)_2Cl]Cl_2$, by boiling an aq. soln. of one of the isomeric dichloroaquotriamminochlorides, and evaporating the liquid. The violet-red crystals form a red soln. with water. For the conductivity and the action of water, *vide supra*, the triaquotriamminotrichloride. A. Werner and J. von Halban prepared **chromic thiocyanatopentamminodichloride,** $[Cr(NH_3)_5(SCy)]Cl_2$.

F. Frowein, and E. H. Riesenfeld and F. Seemann prepared **chromic dichloroaquotriamminochloride,** $[Cr(NH_3)_3(H_2O)Cl_2]Cl$, by adding conc. hydrochloric acid to a soln. of chromium triamminotetroxide in well-cooled, dil. hydrochloric acid, and allowing the soln. to stand for some time. The reddish-violet, dichroic crystals form a blue soln. with water. If conc. hydrochloric acid is used instead of the dil. acid, a light green soln. is obtained, from which grey, needle-shaped crystals of a second modification of the above chloride separate, which is scarcely soluble in cold water, but dissolves in hot water to a red soln. A third modification is obtained by heating a hydrochloric acid soln. of the first chloride for some time at 60°. The soln. gradually becomes green in colour, and on evaporation in a desiccator, dark green crystals are obtained which dissolve in water to a green soln. None of these three chlorides readily loses water, which is therefore probably contained in the complex in all three salts. In all probability they are stereoisomerides:







At present it is impossible to say which formula corresponds with which isomeride. For the electrical conductivity, and hydrolysis, *vide supra*, the triaquotriamminotrichloride. F. Pintus prepared complexes with alcohol, $[Cr(C_2H_5.OH)_3Cl_3]$, and with thiourea, $[Cr(C_3SN_2H_4)_3Cl_3]$.

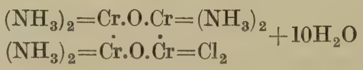
A. Werner and J. L. Klein, and A. Werner and J. V. Dubsky prepared **chromic dihydroxydiaquodiamminochloride,** $[Cr(OH)_2(H_2O)_2(NH_3)_2]Cl.H_2O$, by adding ammonia or pyridine to a conc. aq. soln. of the tetraquodiamminochloride; or by treating the bromide of the series with rubidium chloride. The crystals are lilac or reddish-violet. R. F. Weinland and co-workers, and A. Recoura also prepared the corresponding sulphate. P. Pfeiffer, and P. Pfeiffer and W. Osann prepared **chromic dihydroxydiaquodipyridinochloride,** $[CrPy_2(H_2O)_2(OH)_2]Cl$; and E. Weinmann, **chromic dihydroxydiaquoethylenediaminochloride,** $[Cr(H_2O)_2en(OH)_2]Cl$. A. Werner and J. L. Klein obtained **chromic dichlorodiaquodiamminochloride,** $[Cr(H_2O)_2(NH_3)_2Cl_2]Cl$, in pale green plates by the action of chlorine on a 25 per cent. aq. soln. of the tetrathiocyanatodiammine. The salt is soluble in water and with silver nitrate only one-third of the chlorine is precipitated. P. Pfeiffer and P. Koch, P. Pfeiffer and W. Stern, P. Pfeiffer and A. Trieschmann, and P. Pfeiffer prepared **chromic cis-dichlorobisethylenediaminochloride,** $[Cr\,en_2Cl_2]Cl.H_2O$, and a complex with antimonic and platinic chlorides; P. Pfeiffer, and P. Pfeiffer and P. Koch also prepared the **trans-salt**—anhydrous, monohydrate, hydrochloride, and chloroplatinate. A. Werner obtained **chromic dichloroaquotriamminochloride,** $[Cr(NH_3)_3(H_2O)Cl_2]Cl$, as well as the corresponding iodide, sulphate, and nitrate. P. Pfeiffer and M. Tapuach obtained **chromic dichlorodiaquodipyridinochloride,** $[CrPy_2(H_2O)_2Cl_2]Cl$, and a complex with pyridinium chloride, as well as the bromide, and nitrate. A. Werner and A. Gubser, P. Pfeiffer, N. Bjerrum, and R. F. Weinland and K. Feige discussed **chromic tetraquodichlorochloride,** $[Cr(H_2O)_4Cl_2]Cl$, previously described. P. Pfeiffer and M. Tilgner prepared **chromic dithiocyanatotetramminochloride,** $[Cr(NH_3)_4(SCy)]Cl$; P. Pfeiffer and P. Koch, **chromic cis-dithiocyanatobisethylenediaminochloride,** $[Cr\,en_2(SCy)_2]Cl.H_2O$, and also the

trans-salt ; and P. Pfeiffer and S. Basci, **chromic oxalatotetramminochloride,** $[Cr(NH_3)_4(C_2O_4)]Cl$.

O. T. Christensen prepared **chromic hydroxydecamminopentachloride,** $[Cr_2(NH_3)_{10}(OH)]Cl_5.H_2O$, by treating the corresponding bromide with hydrochloric acid (1 : 1) ; and by the action of air on an ammoniacal soln. of ammonium chloride and chromic chloride. It was also obtained by P. Pfeiffer. J. Petersen gave for the average mol. wt. by the f.p. process 308, when the theoretical value is 469·5 ; and from the electrical conductivity process, the molecule furnishes 5·85 ions in dil. soln. A complex chloroplatinate, and a chloroiodide, were also prepared. S. M. Jörgensen prepared **chromic trihydroxyaquohexamminotrichloride,** $[Cr_2(OH)_3(H_2O)(NH_3)_6]Cl_3.H_2O$, as follows :

> A soln. of chromous chloride, prepared by reducing a soln. of potassium dichromate with zinc and hydrochloric acid, is forced by hydrogen press. into a vessel containing a mixture of 700 grms. ammonium chloride, and 750 c.c. of aq. ammonia, sp. gr. 0·91. The vessel, entirely filled with this mixture, is closed by a stopper through which passes a delivery tube opening under water. The vessel is surrounded by cold water to moderate the reaction. The evolution of hydrogen takes place slowly, and ceases in about 24 hrs. The undissolved ammonium chloride is covered with trihydroxyaquohexamminotrichloride, a portion of which is also contained in the soln. from which it may be precipitated by alcohol ; the precipitate is washed with alcohol, and dried.

The salt was also prepared by P. Pfeiffer. J. Petersen found the mol. wt. 340 to 406 by the f.p. method—theoretical 364·5, and the electrical conductivity indicated that 3·76 ions per mol. are formed. The carmine-red prisms slowly lose a mol. of water over sulphuric acid ; at 100°, the salt gradually decomposes ; 100 parts of water at 18° dissolve 9·4 grms. of salt ; it is decomposed by boiling water ; boiling hydrochloric acid forms aquochlorotetramminochloride ; conc. hydrobromic acid precipitates the bromide ; solid potassium iodide, the iodide ; dil. sulphuric acid followed by alcohol precipitates the sulphate ; ammonium sulphate gives no precipitate ; hydrofluosilicic acid gives a red precipitate ; hydrochloroplatinic acid, forms acicular crystals ; hydrochloric acid, a reddish-brown precipitate ; potassium dichromate, an orange-yellow precipitate ; sodium pyrophosphate, a pale red precipitate soluble in excess ; sodium hydrophosphate, no precipitate ; ammonium thiocyanate, rhombic plates ; potassium ferrocyanide, lilac-coloured precipitate ; and potassium ferricyanide, a brown precipitate. P. Pfeiffer and W. Vorster prepared **chromic hexahydroxysexiesethylenediaminehexachloride,** $[Cr_4(OH)_6en_6]Cl_6.6H_2O$. M. Z. Jovitschitsch prepared **chromic dioxyhexamminodichloride,** $Cr_4O_2(NH_3)_6Cl_2.10H_2O$, by dissolving the precipitate, obtained by adding ammonia to a chromic salt, in an excess of ammonia, and adding hydrochloric acid, and then alcohol. The violet-red precipitate is soluble in water, but only after standing a few hours will the soln. give a precipitate with silver nitrate. It is assumed that the salt is constituted :



$$\begin{array}{l}(NH_3)_2{=}Cr.O.Cr{=}(NH_3)_2\\ \qquad\quad\ \vdots\qquad\ \vdots\\ (NH_3)_2{=}Cr.O.Cr{=}Cl_2\end{array}+10H_2O$$

A. Werner found that when chromium triamminotetroxide, $CrO_4(NH_3)_3$, is added to cold, conc. hydrochloric acid, a grey or bluish-grey precipitate is formed —probably a mixture of chromium triamminodichloroaquochloride and triamminotrichloride—and the filtrate, on standing for two days, deposits chromium triamminotrichloride, $Cr(NH_3)_3Cl_3$, in dark blue crystals, tinged with green. The X-ray spectra of this salt and the corresponding pyridine salt $[Cr(Py)_3Cl_3]$, were studied by O. Stelling. According to A. Werner, the trichlorotriammine is almost insoluble in cold water ; it dissolves in hot water forming a blue soln. which furnishes a series of chromium **triamminodichloroaquo-salts** when treated with the appropriate reagents.

Thus, **chromium triamminodichloroaquochloride,** $[Cr(H_2O)(NH_3)_3Cl_2]Cl$, is formed in brown-leaflets which give a blue soln. with water. The salt is also obtained by the action of conc. hydrochloric acid in the presence of glacial acetic acid on chromium triamminotetroxide. There are also **chromium triamminodichloroaquonitrate,** $[Cr(H_2O)(NH_3)_3Cl_2]NO_3$; **chromium triamminodichloroaquosulphate,** $[Cr(H_2O)(NH_3)_2Cl_2)_2SO_4$; **chromium triamminodichloroaquoiodide,** $[Cr(H_2O)(NH_3)_2Cl_2]I$; the basic iodide, **chromium triamminotriaquodihydroxyiodide,** $[Cr(H_2O)_3(NH_3)_3](OH)_2I$, and **chromium triamminotriaquotribromide,** $[Cr(H_2O)_3(NH_3)_3]Br_3$.

H. I. Schlesinger and R. K. Worner heated chromium chloropentamminochloride in air, hydrogen, carbon dioxide, or ammonia, and found that it furnishes chromium triamminotrichloride. Unless the temp. is carefully controlled, the reaction proceeds further. The black substance, reported by C. E. Ufer, and H. Schrötter, is formed. If the pentammine is heated in a stream of dry hydrogen chloride, a very rapid reaction occurs at about 270° with considerable evolution of heat and is accompanied by a marked colour change of the material from pink to green. If heating is discontinued at this point, the product washed with cold water to which a little hydrochloric acid has been added, and then dried with alcohol and ether, a very insoluble green substance, chromium trichlorotriammine is obtained. The triammine differs from that prepared by A. Werner. His compound is blue-green, dissolves fairly readily in warm water and especially easily in warm dil. hydrochloric acid to give a deep blue soln. of trichloroaquotriamminochloride ; that of A. Werner is insoluble in hydrochloric acid or in water, but with the latter it slowly reacts to give a pink soln. which has since been shown to contain chromic diaquotetramminochloride. Here evidently is a case of isomerism of a type not frequently encountered, but whether it is stereoisomerism, possible according to A. Werner's theory, or is what is often called " polymerization isomerism," cannot be decided because of the insolubility of the compounds in question. Attempts to remove some of the three remaining molecules of ammonia from the co-ordination sphere show the firmness with which chromium retains the co-ordination number 6. When the triammine is heated to 175° in a stream of hydrogen chloride, ammonia is not withdrawn from the compound, but hydrogen chloride is quantitatively absorbed to give a reddish-purple very hygroscopic crystalline material which may be considered to be **ammonium chromic hexachloride,** $(NH_4)_3[CrCl_6]$. The substance is insoluble in all solvents except water, with which it reacts almost instantly to produce a deep green soln. presumably of hydrated chromic chloride. In favour of the argument that the ammonium compound is a salt of the complex ion $[CrCl_6]'''$, anhydrous chromic chloride, alone or when mixed with ammonium chloride, reacts with liquid ammonia to give a mixture of hexammine and chloropentammine chromic chlorides without the intermediate formation of a soln. What is called ammonium chromic hexachloride dissolves readily in liquid ammonia to give a green soln. which is transformed to the pentammine only after complete evaporation of the liquid. Anhydrous chromic chloride reacts exceedingly slowly with dry gaseous ammonia ; the new compound reacts rapidly at ordinary temp. to give the pentammine. Double salts should possess a colour which is the summation of the colours of the constituent salts ; the compound here prepared is decidedly different in colour from any known form of chromic chloride, the only coloured constituent. In this instance, then, chromium, rather than changing its co-ordination number as the result of removal of ammonia, takes up hydrogen chloride, and the ammonia, although removed from the co-ordination sphere, remains in the molecule. If the triamminotrichloride is treated with oxalic acid or an oxalate, **ammonium chromium triammino - oxalatochloride,** $(NH_4)_6[Cr_2(NH_3)_3(C_2O_4)Cl_{10}]$, is formed.

A. Johnsen[2] obtained no isomorphous mixtures of ammonium chloride and violet chromic chloride, but with green hexahydrated chromic chloride, the ammonium chloride crystals are coloured green. J. W. Retgers obtained solid soln. of both green and violet chromic chlorides from aq. soln. N. Larsson prepared **ammonium chromium tetrachloride,** $NH_4Cl.CrCl_3.6H_2O$, or $[CrCl(H_2O)_5]Cl_2.NH_4Cl.H_2O$, by boiling a soln. of a mixture of chromic chloropentaquodichloride and ammonium chloride, and passing hydrogen chloride through the soln. cooled by a freezing mixture. G. Neumann prepared **ammonium chromic pentachloride,** $2NH_4Cl.CrCl_3.H_2O$, or $(NH_4)_2[CrCl_5(H_2O)]$, by adding ammonium chloride to a soln. of chromic chloride in 96–97 per cent. alcohol, and passing hydrogen chloride through the liquid heated on a water-bath with a reflux condenser. The violet, hygroscopic crystals of the *monohydrate* are probably rhombic. They are decomposed by water. A. Werner and A. Gubser represent this series of salts by $[Cr(H_2O)Cl_5](NH_4)_2$. R. F. Weinland and T. Schumann found that when hydrogen chloride is passed into an ice-cold soln. of equimolar proportions of green hexahydrated chromic chloride and ammonium chloride, green rectangular plates of the *hexahydrate* are formed. The salt is deliquescent, and turns red when warmed. A soln. of the salt acidified with nitric acid, and treated with silver nitrate deposits three-fifths of the chlorine as silver chloride. Hence the constitution of the salt is taken to be $(NH_4)_2[Cr(H_2O)_4Cl_2]Cl_3.2H_2O$. H. I. Schlesinger and R. K. Worner prepared **ammonium chromic hexachloride,** $(NH_4)_3CrCl_6$, in hygroscopic crystals, by heating chromic trichlorotriammine in hydrogen chloride at 175°. It reacts with ammonia to furnish chromic chloropentamminodichloride.

F. Ephraim and W. Ritter found that ammonia acts on potassium chromic aquopentachloride forming a greyish-violet mass of chromic hydroxypentamminochloride. This dissolves in water, and nitric acid precipitates from the cherry-red soln., first chromium nitratopentamminodinitrate, and then chromic nitrataquotetramminodinitrate in a 27 per cent. yield; while hydrochloric acid precipitates from the cherry-red soln., the chloropentamminochloride in 40 per cent. yield. Similar results were obtained with the ammonium salt. F. Ephraim and W. Ritter suggest that ammonium hydroxypentachloride is formed as an intermediate compound. No evidence was obtained of the formation of ammines of the double salts.

A. Werner and A. Gubser[3] obtained **lithium chromium pentachloride,** $2LiCl.CrCl_3.5H_2O$, that is, $Li_2[Cr(H_2O)Cl_5].4H_2O$, as in the case of the ammonium salt, by passing hydrogen chloride into a soln. of 5 grms. of lithium chloride, and 17 grms. of hexahydrated chromic chloride. The red, hygroscopic powder is easily soluble in alcohol forming a green soln.; with water, the soln. is transiently red. At 0°, the salt gives no precipitate with silver nitrate when that salt is first added. N. Larsson found that **lithium chloropentaquodichloride,** $[CrCl(H_2O)_5]Cl_2.LiCl.nH_2O$, prepared as in the case of the ammonium salt, is very hygroscopic. J. J. Berzelius reported that when a soln. of sodium dichromate, hydrochloric acid, and alcohol is evaporated on the water-bath, a green mass of **sodium chromium tetrachloride,** $NaCrCl_4$, is formed, and it becomes violet on a sand-bath; N. Larsson obtained the salt **sodium chlorotetraquodichloride,** $[CrCl_2(H_2O)_4]Cl_2.NaCl.nH_2O$, as in the case of the sodium salt. J. J. Berzelius also prepared reddish-violet crystals of **potassium chromium tetrachloride,** $KCrCl_4$, in a similar manner; and found that the salt is decomposed when the aq. soln. is evaporated. L. Godefroy regarded this salt as a mixture of the pentachloride with chromic chloride. N. Larsson did not obtain $[CrCl(H_2O)_5]Cl_2.KCl.nH_2O$ by the method employed for the ammonium salt. L. Godefroy prepared **potassium chromium pentachloride,** $K_2CrCl_5.H_2O$, or $K_2[Cr(H_2O)Cl_5]$, by passing chlorine for 5 or 6 hrs. through a soln. of 300 grms. of powdered potassium dichromate and 700 grms. of alcohol; and G. Neumann obtained it by passing hydrogen chloride through a soln. of chromic and potassium chlorides in 96 to 97 per cent. alcohol warmed on a water-bath. The reddish, or violet-red crystalline powder is stable in air; it can be crystallized by heating it with 40 per cent. hydrochloric acid in a sealed tube at 120° to 130°. The crystals are probably rhombic; very hygroscopic; and are decomposed by water, forming potassium chloride and an oxychloride. For the action of ammonia, *vide supra,* the ammonium salt. J. J. Berzelius treated sodium chromium tetrachloride with alcohol, and obtained rose-red **sodium chromium hexachloride,** Na_3CrCl_6.

E. Zettnow, and J. J. Berzelius obtained **potassium chromium hexachloride,** K_3CrCl_6, in an analogous manner ; and E. Frémy, found that when a mixture of potassium dichromate, mixed with charcoal, is heated in chlorine gas, chromic chloride sublimes, and the hexachloride remains. The salt is soluble in water, and at the same time is decomposed into its constituent chlorides. L. Godefroy said that the hexachloride is really a mixture of the pentachloride and potassium chloride.

N. Larsson prepared **rubidium chromium tetrachloride,** $RbCl.CrCl_3.5H_2O$, or $[CrCl(H_2O)_5]Cl_2.RbCl$, as in the case of the corresponding ammonium salt ; and similarly with **cæsium chromium tetrachloride,** $CsCl.CrCl_3.5H_2O$, or $[CrCl(H_2O)_5]Cl_2.CsCl$. G. Neumann prepared **rubidium chromium pentachloride,** $Rb_2CrCl_5.H_2O$, or $Rb_2[Cr(H_2O)Cl_5]$, by the method employed for the potassium salt ; and A. Werner and A. Gubser, by passing hydrogen chloride into a soln. of the constituent chlorides. The *monohydrate* furnishes reddish-violet crystals, sparingly soluble in cold water ; and readily soluble in hot water forming a green soln. By working with the soln. at 0°, A. Werner and A. Gubser obtained the *octohydrate*, $[(ClRb.Cl)_2Cr(H_4O_2)_4]Cl$, in green, prismatic crystals, which lose water when confined over sulphuric acid, and deliquesce with decomposition in air. Only three-fifths of the chlorine is at first precipitated by silver nitrate. N. Larsson prepared the compound $[CrCl_2(H_4O_2]Cl.2RbCl$ from a soln. of chromic dichloroaquochloride and rubidium chloride, cooled with a freezing mixture, and treated with hydrogen chloride. It is stable in air ; alcohol extracts chromic chloride ; at 85° it forms $Rb_2[CrCl_5(H_2O)]$. H. L. Wells and B. B. Boltwood prepared **cæsium chromium pentachloride,** $Cs_2CrCl_5.H_2O$, or $Cs_2Cr(H_2O)Cl_5$, by passing hydrogen chloride into a warm soln. of the component chlorides. The *monohydrate* forms violet crystals which are stable in air, and do not lose water at 160°. They dissolve slowly in water forming a green soln. which, on evaporation, yields crystals of the *tetrahydrate* which A. Werner and A. Gubser represent by the formula $(ClCsCl)_2Cr(H_2O)_4Cl$, because only three-fifths of the chlorine is at first precipitated by silver nitrate. This subject was discussed by R. F. Weinland and A. Koch. H. St. C. Deville obtained green crystals by fusing a mixture of chromic and sodium chlorides.

S. M. Jörgensen prepared **chromic hydroxydecamminotrichlorodichloraurate,** $[Cr_2(OH)(NH_3)_{10}]Cl_3(AuCl_4)_2$, in reddish-yellow needles by treating a soln. of $[Cr_2(OH)(NH_3)_{10}]Cl_5.H_2O$ with an aq. soln. of chlorauric acid. It loses its water of crystallization at 100° ; and the salt is sparingly soluble in water. S. M. Jörgensen also prepared reddish-brown needles of **chromic trihydroxyaquohexamminochlorodichloraurate,** $[Cr(OH)_3(H_2O)(NH_3)_6]Cl(AuCl_4)_2$, from $[Cr_2(OH)_3(H_2O)(NH_3)_6]Cl_3.H_2O$, in an analogous manner. It loses a mol of water over sulphuric acid.

G. Neumann obtained **beryllium chromium pentachloride,** $BeCrCl_5.H_2O$, by the method used in connection with the analogous potassium salt. He prepared **magnesium chromium pentachloride,** $MgCrCl_5.H_2O$, in a similar way. S. M. Jörgensen prepared the complex **chromic hexamminotrichloromercurichloride,** $[Cr(NH_3)_6]Cl_3.HgCl_2$. According to O. T. Christensen, when a conc. aq. soln. of aquopentamminotrichloride is treated with mercuric chloride, yellowish-red, sparingly soluble **chromic aquopentamminotrichlorotrismercurichloride,** $[Cr(NH_3)_5(H_2O)]Cl_3(HgCl_2)_3.H_2O$, is formed. He also prepared yellowish-red needles of **chromic nitritopentamminodichlorobismercurichloride,** $[Cr(NH_3)_5(NO_2)]Cl_2(HgCl_2)_2$. S. M. Jörgensen similarly obtained **chromic chloropentamminodichlorotrismercurichloride,** $[Cr(NH_3)_5Cl]Cl_2(HgCl_2)_3$, in rose-red needles ; and P. T. Cleve, **chromic aquochlorotetramminodichlorotrismercurichloride,** $[Cr(NH_3)_4(H_2O)Cl]Cl_2(HgCl_2)_3$, in rose-red plates. G. Neumann prepared **thallous chromium hexachloride,** Tl_3CrCl_3, in hygroscopic, violet crystals, by the process used for potassium chromium pentachloride. R. F. Weinland and E. Gussmann prepared **chromic hexacetatohydroxyaquotripyridinochlorostannate,** $[Cr_3(CH_3COO)_6Py_3(H_2O)(HO)]SnCl_6.7H_2O$, in pale grey needle-like crystals, from the acetate of the series and sodium chlorostannate.

P. Pfeiffer and M. Tapuach prepared **chromic cis-dichlorobisethylenediaminochloroantimonate,** [Cr en_2Cl_2]$SbCl_6$, from the chloride of the series and a hydrochloric acid soln. of antimony pentachloride.

REFERENCES.

[1] S. M. Jörgensen, *Journ. prakt. Chem.*, (2), **20**. 105, 1879; (2), **25**. 88, 330, 1882; (2), **30**. 12, 1884; (2), **42**. 206, 1890; (2), **45**. 260, 1892; O. T. Christensen, *ib.*, (2), **23**. 28, 1881; (2), **24**. 15, 1881; (2), **30**. 1, 1884; *Zeit. anorg. Chem.*, **4**. 229, 1893; R. Klement, *ib.*, **160**. 165, 1927; I. Koppel, *ib.*, **28**. 461, 1901; A. Hiendlmayr, *Beiträge zur Chemie der Chrom- und Kobalt-Ammoniake*, Friesing, 1907; W. Biltz and E. Birk, *Zeit. anorg. Chem.*, **134**. 125, 1924; F. Frowein, *ib.*, **110**. 107, 1920; J. Petersen, *Zeit. phys. Chem.*, **10**. 582, 1892; E. Rosenbohm, *ib.*, **93**. 693, 1919; N. Bjerrum, *ib.*, **59**. 581, 1907; *Ber.*, **40**. 2917, 1907; **43**. 2290, 1910; A. Werner and A. Miolati, *Zeit. phys. Chem.*, **14**. 515, 1894; J. L. Klein, *Liebig's Ann.*, **35**. 283, 1902; *Ueber Tetraquodiammin- und Diacidodiaquo-diammin-Chromsalze*, Zürich, 1902; A. Werner, *Ber.*, **39**. 2656, 2665, 1906; **43**. 2286, 2290, 1910; A. Werner and J. L. Klein, *Ber.*, **35**. 287, 1902; A. Werner and R. Huber, *ib.*, **39**. 336, 1906; A. Werner and J. von Halban, *ib.*, **39**. 2671, 1906; J. von Halban, *Untersuchungen über Chromammoniakverbindungen*, Zürich, 1902; J. V. Dubsky, *Ueber basische Salze, deren Zusammensetzung und Beziehungen*, Zürich, 1908; A. Werner and J. V. Dubsky, *Ber.*, **40**. 4091, 1907; A. Werner and A. Gubser, *ib.*, **34**. 1591, 1901; F. Ephraim and W. Ritter, *Helvetica Chim. Acta*, **11**. 848, 1928; A. Gubser, *Ueber die Hydrate des Chromchlorids*, Zürich, 1900; P. Pfeiffer, *Liebig's Ann.*, **342**. 283, 1906; *Zeit. anorg. Chem.*, **24**. 288, 1904; **31**. 418, 1902; **36**. 349, 1903; **56**. 261, 1907; **29**. 134, 1901; *Ber.*, **29**. 131, 1901; **33**. 2689, 1900; **34**. 2560, 1901; **36**. 1927, 1903; **37**. 4255, 1904; **39**. 1874, 1906; **40**. 3130, 1907; P. Pfeiffer and S. Basci, *ib.*, **38**. 3594, 1905; S. Basci, *Beitrag zur Chemie ammoniakalischer Chromsalze*, Zürich, 1907; M. Tapuach, *Zur Kenntnis der Hydratisomerie bei Di- und Trihalogenochromsalzen*, Zürich, 1907; P. Pfeiffer and M. Tapuach, *Ber.*, **39**. 1893, 1906; P. Pfeiffer and W. Osann, *ib.*, **39**. 1873, 2121, 1906; **40**. 4031, 1907; E. Weinmann, *Diammidoverbindungen mit besonderer Rücksichtnahme auf die Tetrarhodanatodiammidochromi-Salze*, Zürich, 1919; A. Trieschmann, *Beitrag zur Stereoisomerie und Koordinationsisomerie bei Chromsalzen*, Zürich, 1906; P. Pfeiffer and A. Trieschmann, *Ber.*, **37**. 4288, 1904; *Liebig's Ann.*, **342**. 294, 1906; P. Pfeiffer and P. Koch, *Ber.*, **37**. 4268, 4282, 1904; *Zeit. anorg. Chem.*, **56**. 293, 1907; A. Benrath, *ib.*, **177**. 286, 1928; P. Koch, *Beitrag zur Stereoisomerie der Chromsalze*, Zürich, 1905; P. Pfeiffer and M. Tilgner, *Zeit. anorg. Chem.*, **55**. 367, 1907; R. Stern, *Beitrag zur Chemie der Aquo-chromsalze*, Zürich, 1908; P. Pfeiffer and R. Stern, *Zeit. anorg. Chem.*, **58**. 240, 1908; P. Pfeiffer and R. Prade, *ib.*, **58**. 249, 1908; P. Pfeiffer and W. Vorster, *ib.*, **58**. 287, 1908; R. Krebs, *Über Chromchloridsulfate und Chromsulfate*, Tübingen, 1906; R. F. Weinland and R. Krebs, *Zeit. anorg. Chem.*, **59**. 581, 1907; R. F. Weinland and K. Feige, *ib.*, **36**. 244, 1903; T. Schumann, *Ueber Chromiaquoverbindungen*, Tübingen, 1908; R. F. Weinland and T. Schumann, *Ber.*, **40**. 3091, 1907; E. H. Riesenfeld and F. Seemann, *ib.*, **42**. 4231, 1909; F. Seemann, *Über Chromi-aquo-Triammine*, Freiburg, 1910; P. T. Cleve, *Oefvers. Akad. Förh.*, 165, 1861; *Svenska Akad. Handl.*, **6**. 4, 1865; *Lärobok i oorganisk Kemi*, Stockholm, 307, 1873; W. R. Lang and C. M. Carson, *Journ. Amer. Chem. Soc.*, **26**. 414, 1904; A. Recoura, *Bull. Soc. Chim.*, (3), **27**. 1156, 1902; S. Guralsky, *Ueber Di- und Triamminchromisalze*, Zürich, 1909; R. F. Weinland, *Ber.*, **41**. 3237, 1908; **42**. 3828, 1909; M. Z. Jovitschitsch, *Monatsh.*, **34**. 225, 1913; *Compt. Rend.*, **158**. 872, 1914; *Helvetica Chim. Acta*, **3**. 40, 1920; H. J. S. King, *Journ. Chem. Soc.*, **125**. 1329, 1924; **127**. 2100, 1925; A. B. Lamb and J. W. Marden, *Journ. Amer. Chem. Soc.*, **33**. 1873, 1911; H. Freundlich and H. Pape, *Zeit. phys. Chem.*, **86**. 458, 1914; H. Freundlich and R. Bartels, *ib.*, **101**. 177, 1922; F. Ephraim and P. Mosimann, *Ber.*, **55**. B, 1608, 1922; Y. Shibata, *Journ. Coll. Science Tokyo*, **41**. 6, 1919; H. Lessheim, J. Meyer and R. Samuel, *Zeit. Physik*, **43**. 299, 1927; E. Birk, *Zeit. anorg. Chem.*, **164**. 241, 1927; S. Aoyama, K. Kimura and Y. Nishina, *Zeit. Physik*, **44**. 810, 1927; L. A. Welo, *Phil. Mag.*, (7), **6**. 481, 1928; O. Stelling, *Zeit. Elektrochem.*, **34**. 520, 1928; F. Pintus, *Ueber die Existenz des einwertigen Chroms und den Einfluss der Komplexkonstitution auf die Bildung chromorganischer Verbindungen*, Leipzig, 1928; C. E. Ufer, *Liebig's Ann.*, **112**. 281, 1859; H. Schrötter, *ib.*, **37**. 148, 1841; H. I. Schlesinger and R. K. Worner, *Journ. Amer. Chem. Soc.*, **51**. 3520, 1929; H. I. Schlesinger and D. N. Rickles, *ib.*, **51**. 3523, 1929; E. Frémy, *Compt. Rend.*, **47**. 886, 1858.

[2] G. Neumann, *Liebig's Ann.*, **244**. 339, 1888; R. F. Weinland and T. Schumann, *Ber.*, **40**. 3770, 1907; A. Werner and A. Gubser, *ib.*, **34**. 1603, 1901; *Liebig's Ann.*, **322**. 345, 1902; J. W. Retgers, *Zeit. phys. Chem.*, **9**. 390, 1892; A. Johnsen, *Neues Jahrb. Min.*, ii, 113, 1903; N. Larsson, *Zeit. anorg. Chem.*, **110**. 153, 1920; F. Ephraim and W. Ritter, *Helvetica Chim. Acta*, **11**. 848, 1928; H. I. Schlesinger and R. K. Worner, *Journ. Amer. Chem. Soc.*, **51**. 3520, 1929.

[3] A. Gubser, *Ueber die Hydrate des Chromchlorids*, Zürich, 1900; A. Werner and A. Gubser, *Ber.*, **34**. 1603, 1901; P. T. Cleve, *Oefvers. Akad. Förh.*, 171, 1861; *Svenska Akad. Handl.*, **6**. 4, 1865; J. J. Berzelius, *Oefvers. Akad. Förh.*, 206, 1844; E. Zettnow, *Pogg. Ann.* **143**. 477, 1871; L. Godefroy, *Bull. Soc. Chim.*, (2), **40**. 170, 1883; (2), **42**. 194, 1884; *Compt. Rend.*, **99**. 141, 1884; H. St. C. Deville, *ib.*, **43**. 971, 1856; E. Frémy, *Ann. Chim. Phys.*, (3), **21**. 361, 1844; G. Neumann, *Liebig's Ann.*, **244**. 194, 1888; H. L. Wells and B. B. Boltwood, *Amer.*

Journ. Science, (3), **50**. 249, 1895 ; *Zeit. anorg. Chem.*, **10**. 181, 1895 ; N. Larsson, *ib.*, **110**. 153, 1920 ; A. Werner, *ib.*, **19**. 176, 1899 ; R. F. Weinland and A. Koch, *ib.*, **39**. 323, 1904 ; R. F. Weinland and E. Gussmann, *ib.*, **67**. 167, 1910 ; S. M. Jörgensen, *Journ. prakt. Chem.*, (2), **20**. 131, 1879 ; (2), **25**. 333, 1882 ; (2), **45**. 266, 1892 ; O. T. Christensen, *ib.*, (2), **23**. 45, 1881 ; (2), **24**. 88, 1881 ; P. Pfeiffer and M. Tapuach, *Ber.*, **39**. 1893, 1906.

§ 26. Chromium Bromides and Oxybromides

A. Moberg[1] observed the formation of a dark green mixture when chromous chloride is treated with potassium bromide ; but the product was not examined. F. Wöhler, M. Bauck, and H. Moissan observed that **chromous bromide,** or **chromium dibromide,** $CrBr_2$, is formed by passing hydrogen over heated chromic bromide ; and H. Moissan also obtained it by the action of dry hydrogen bromide on chromium at a high temp. ; and by passing a mixture of bromine vapour and nitrogen over an excess of chromium at a red-heat. An aq. soln. of chromous bromide is formed by reducing a soln. of chromic bromide with zinc and hydrobromic acid. W. Biltz and E. Birk gave 4·356 for the sp. gr. at 25°/4°. According to A. Moberg, H. Moissan, F. Wöhler, and M. Bauck, white, crystalline chromous bromide readily fuses to a yellow liquid ; it forms a blue soln. with water, and the soln. quickly absorbs oxygen. The salt rapidly deliquesces in air forming green chromic bromide. The salt is soluble in alcohol. The presence of a trace of chromous bromide will bring anhydrous chromic chloride, bromide, or iodide into soln.—*vide supra*, chromic chloride. W. Biltz and E. Birk gave 1·714 for the sp. gr. of **chromous hexamminobromide,** $CrBr_2.6NH_3$, at 25°/4°. W. Traube and W. Passarge found that with hydrazine, chromous bromide forms **chromous dihydrazinobromide,** $CrBr_2.2N_2H_4$.

A. J. Balard obtained a soln. of **chromic bromide,** $CrBr_3$, by the action of bromine-water on the green hydrated chromic oxide, and the filtrate, when concentrated by evaporation, deposits green crystals—presumably the hydrate (*q.v.*). C. Löwig found that if lead chromate be boiled with hydrobromic acid, a dark green soln. is obtained ; he could not get the conc. soln. to crystallize, and he obtained a yellowish-red powder on evaporation. J. J. Berzelius used silver chromate in place of the lead salt. J. B. Berthemot obtained a soln. of the salt by the action of hydrobromic acid on chromic acid, in which case bromine is evolved ; he found that the green aq. soln. of chromic bromide turns brown on evaporation, and crystallizes with difficulty ; if further evaporated, the residue evolves hydrobromic acid. He prepared the anhydrous bromide by the action of bromine vapour on heated chromium—the combination is attended incandescence ; H. Moissan obtained it in an analogous way. F. Wöhler, and M. Bauck prepared it, as in the analogous case of chromic chloride, by the action of bromine vapour on a heated mixture of chromic oxide and carbon. F. Bourion prepared the bromide by passing the vapour of sulphur monochloride in a slow current of hydrogen bromide over chromic oxide at 135°, and finishing off with hydrogen bromide alone. The black plates or scaly crystals of chromic bromide appear olive-green by reflected light, and there is a pleochroic red colour as well. The powder is yellowish-green. W. Biltz and E. Birk gave 4·250 for the sp. gr. at 25°/4°. According to F. Wöhler, M. Bauck, and F. Bourion, when the anhydrous tribromide is heated in air, chromic oxide is formed ; in hydrogen, chromous bromide. The anhydrous salt appears to be insoluble in water, but it forms a green aq. soln. if a trace of chromous bromide be present. Chromic bromide deliquesces when exposed on tin-foil forming a green soln. The salt is soluble in boiling water ; alkali-lye decomposes it more easily than is the case with the chloride.

L. Varenne reported crystals of the *octohydrate*, $CrBr_3.8H_2O$, to be formed by treating a cold, conc. soln. of potassium or ammonium trichromate with dil. hydrobromic acid, and allowing the liquor to stand at 0°. The violet crystals are a combination of the cube and octahedron. The salt loses water at 110° and becomes green ; at 200°, in air, it forms an oxybromide, and finally chromic oxide. A. Werner and A. Gubser could not confirm these results. Chromic bromide furnishes a *hexahydrate* which occurs in two isomeric forms—green, and violet. The facts in connection with the isomeric hexahydrates of chromic chloride are applicable to the bromide. The **green hexahydrate** is considered to be **chromic dibromohexaquobromide,** $[(H_2O.Br)_2Cr(H_2O)_4]Br$, or $[Cr(H_2O)_4Br_2]Br.2H_2O$. A. Recoura obtained it by evaporating a sat. soln. of chromic oxide with a large excess of hydrobromic acid; and A. Werner and A. Gubser recommended passing hydrogen bromide over the evaporating soln. The green, hygroscopic crystals are acicular or tabular, which have, according to R. F. Weinland and A. Koch, the same optical properties as the green chloride, but it is rather stronger yellow tinge. A. Byk and H. Jaffe studied the violet and ultra-violet absorption spectrum of aq. soln. C. S. Garrett examined the effect of the chlorides of lithium, potassium, calcium, zinc, mercury, and aluminium on the mol. extinction of soln. of chromic bromide after standing 3 days, and 3½ months. The results are said to make it appear as if the water mols. play an initial part in changing the complex to the simple configuration, and that following this a second reaction sets in tending again to the formation of complexes owing to the presence of the colourless haloids in the soln. When, however, the colourless haloids have decidedly dehydrating properties, the hydration on dilution is initially inhibited, although the final point reached, when an excess of water mols. is present, is independent of the hygroscopic properties of the colourless haloid. N. Bjerrum found that the electrical conductivity of a freshly prepared soln. of a mol of the salt in 625 litres of water is 70 to 80 mhos at 0°, and 265·1 mhos at 25°. It forms only two ions, $[Cr(OH)_4Br_2]'$ and Br'. This is in agreement with the observation that only one-third of the bromine is at once precipitated on adding silver nitrate. E. Rosenbohm gave for the magnetic susceptibility, $13{\cdot}96\times10^{-6}$ mass units. A. Werner and A. Gubser found that the transformation of the green into the violet soln. is faster than is the case with the chloride. A. Recoura found that the salt is very soluble in water, and that the heat of soln. is 0·68 Cal. The aq. soln. reacts acid, and has a sweet taste. The salt is easily soluble in alcohol, and insoluble in ether. I. Koppel described a brown alcoholate, $CrBr_3.3C_2H_5OH$, or $[Cr(C_2H_5OH)_3Br_3]$, analogous to the red chloride; and P. Pfeiffer, the complex with pyridinium chloride, $[Cr(H_2O)_3Br_3].2PyHBr$. A. Werner and A. Gubser found that it is soluble in acetone, and precipitated by ether. N. Bjerrum said that it is soluble in fuming hydrobromic acid, but insoluble in a mixture of ether and this fuming acid. J. M. Ordway found that the aq. soln. of a mol of the salt dissolves 2 mols of the hydrated oxide.

The blue, greyish-blue, or **violet hexahydrate** is symbolized, as in the case of the corresponding hydrate of chromic chloride, by $[Cr(H_2O)_6]Br_3$, that is, **chromic hexaquotribromide.** A. Recoura prepared it by passing hydrogen bromide into a boiling, conc. soln. of the green hexahydrate. The soln. becomes brown, and as it cools, it deposits the violet salt. A. Werner and A. Gubser, and R. F. Weinland and A. Koch dissolved the product in a little water, and again passed hydrogen bromide into the soln. cooled below zero. G. O. Higley obtained the violet hexahydrate by saturating with hydrogen bromide a soln. of 5 grms. of the violet sulphate in 20 c.c. of water at 10°. The greyish-blue or violet powder was found by R. F. Weinland and A. Koch to have the same crystal form as the corresponding chloride. The violet and ultra-violet absorption spectra of the soln. were examined by A. Byk and H. Jaffe. The crystals are hygroscopic, and have a sweet taste. A. Recoura found that it dissolves in water with the development of 14·35 Cals. At 100°, it passes into the green isomer, and the heat of transformation from the green solid to the blue isomer is −2·17 Cals. The heat of the reaction $CrBr_{3\text{violet soln.}}+3NaOH_{\text{aq.}}=3NaCl_{\text{soln.}}+Cr(OH)_3$ is 21·6 Cals. The phenomena associated with the conversion of the green into the blue soln. resemble those in the analogous conversion with the chloride (*q.v.*). The rate of conversion is much greater with the bromide than with the chloride. Thus, the molar conductivity, μ mhos, of a $0{\cdot}008M$-soln., with time is:

1°	Time	0	2	8	25	70	110	160 min.
	μ .	76·7	77·2	94·5	111·1	125·8	136·3	156·1 mhos.
25°	Time	0	2	5	10	20	30	50 min.
	μ .	265·1	288·5	300·7	319·9	322·4	325·1	325·1 mhos.

The transformation to a state of equilibrium is thus completed in 30 min. at 25°, but not in 160 min. at 1°. A. Recoura gave 11·5 Cals. for the complete transformation of a mol of the green salt in soln. In the cold in dil. soln. the violet form is favoured, while an increase of temp., concentration, or the presence of hydrobromic acid favours the green. Unlike the case of the chlorides, N. Bjerrum found that the violet isomer occupies the greater vol. A. Recoura noticed that in concentrating a violet soln. of the bromide, the violet isomer first separates out, while with a violet soln. of the chloride, the dark green form appears. A. Werner and A. Gubser found the mol. conductivity of the violet soln. with a mol of the salt in v litres at 0° is $\mu=173$ mhos when $v=125$ at 0°, and at 25°, when $v=125$, 250, 500, and 1000, $\mu=329{\cdot}5$, 360·3, 391·2, and 431·6 mhos respectively. The results indicate that a mol. of the salt forms four ions when dissolved in water, *viz.*, $[Cr(H_2O)_6]^{\cdots}$ and $3Br'$, and is in agreement with the fact that all the bromine is at once precipitated by silver nitrate. The results are summarized by the formula $[Cr(H_2O)_6]Br_3$. A. Recoura said that the salt is insoluble in alcohol, A. Werner and A. Gubser said that it is soluble in acetone, and insoluble in ether. The hydrated chromic hydroxide precipitated by alkali-lye dissolves in acid forming the violet soln. E. Hein and co-workers studied some complexes with organic radicles.

S. M. Jörgensen[2] found that when a soln. of the hexamminonitrate is treated with conc. hydrobromic acid, and the precipitate is washed with dil. hydrobromic acid and then with alcohol, there is formed orange-yellow, rhombic plates of **chromic hexamminobromide,** $[Cr(NH_3)_6]Br_3$. F. Pintus also prepared this salt. W. Biltz and E. Birk found the sp. gr. to be 2·151 at 25°/4°, and the mol. vol. 183·2. J. Petersen, and P. Pfeiffer found the mol. wt. by the cryoscopic method and the mol. conductivity corresponds with the formation of four ions. H. J. S. King gave for the conductivity, μ mhos, of a mol of the salt in v litres at 25°, $\mu=355{\cdot}5$ for $v=64$; $\mu=391$ for $v=391{\cdot}1$; and $\mu=423{\cdot}3$ for $v=256$. It also forms a complex bromoplatinate. F. Ephraim and W. Ritter found that no ammonia is absorbed by the hexamminotribromide at room temp., but when cooled by a freezing mixture ammonia gas is absorbed, and the decomposition curve of the ammine of the hexamminotribromide is that represented by Fig. 78, and it shows that a triammine and monammine are formed. P. Pfeiffer, and F. Pintus obtained the corresponding **chromic trisethylenediaminotribromide,** $[Cr\,en_3]Br_3.nH_2O$; P. Pfeiffer and H. Pietsch, **chromic bisethylenediaminopropylenediaminotribromide,** $[Cr\,en_2pn]Br_3.3H_2O$; and F. Pintus, **chromium tripyridinotribromide,** $[CrPy_3]Br_3$. H. Farl studied the complexes with pyridine and chromic dichloroethylate. A. Benrath found that in the presence of hydrobromic acid, $[Cr(NH_3)_5Br]Br_2$, and $[Cr(NH_3)_5(H_2O)]Br_3$ are formed. O. T. Christensen prepared **chromic aquopentamminotribromide,** $[Cr(NH_3)_5(H_2O)]Br_3$, from an aq. soln. of the hydroxide and hydrobromic acid (1 : 3). The yellow crystalline powder is soluble in water, and loses a mol. of water at 110°. H. J. S. King also prepared this salt. F. Ephraim and W. Ritter found that the salt absorbs ammonia in the cold, and that the decomposition curve of the product shows the existence of an octammine and a tetrammine. A. Benrath found that the stable phase in the presence of hydrobromic acid is $[Cr(NH_3)_5Br]Br_2$. P. Pfeiffer treated chromic hydroxyaquotetramminodithionate with conc. hydrobromic acid, and obtained a brick-red crystalline powder of **chromic diaquotetramminotribromide,** $[Cr(NH_3)_4(H_2O)_2]Br_3$.

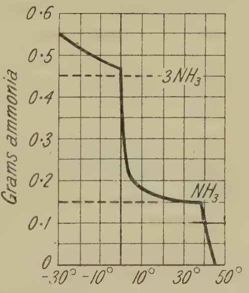


FIG. 78.—Dissociation of the Ammine of Chromic Hexamminotribromide.

P. Pfeiffer and R. Stern prepared **chromic cis-diaquobisethylenediaminotribromide,** $[Cr\,en_2(H_2O)_2]Br_3.2H_2O$; and P. Pfeiffer and R. Prade obtained the **trans-salt.** A. Werner prepared **chromic triaquotriamminotribromide,** $[Cr(H_2O)_3(NH_3)_3]Br_3$, by the action of hydrobromic acid on the hydroxyaquotriamminoiodide; and A. Werner and J. L. Klein, **chromic tetraquodiamminotribromide,** $[Cr(NH_3)_2(H_2O)_4]Br_3$, by the action of hydrobromic acid on the dihydroxydiaquodiamminobromide; P. Pfeiffer, and P. Pfeiffer and M. Tapuach also obtained **chromic tetraquodipyridinotribromide,** $[CrPy_2(H_2O)_4]Br_3.2H_2O$.

H. J. S. King prepared **chromic hydroxypentamminobromide,** $[Cr(NH_3)_5(OH)]Cl_2.\frac{1}{2}H_2O$, as in the case of the corresponding chloride. F. Ephraim and W. Ritter found that the salt absorbs ammonia in the cold but the decomposition curve shows no signs of the formation of a definite ammine. P. Pfeiffer prepared **chromic hydroxyaquotetramminodibromide,** $[Cr(NH_3)_4(H_2O)(HO)]Br_2$, by adding pyridine to a conc. soln. of the diaquotetramminodibromide. P. Pfeiffer, and P. Pfeiffer and R. Stern prepared **chromic cis-hydroxyaquobisethylenediaminodibromide,** $[Cr\,en_2(H_2O)(HO)]Br_2.H_2O$, or $[Cr\,en_2(H_4O_2)(HO)]Br_2$; and P. Pfeiffer and R. Prade prepared the **trans-salt.** O. T. Christensen obtained **chromic nitritopentamminodibromide,** $[Cr(NH_3)_5(NO_2)]Br_2$, by the action of potassium or ammonium bromide on the chloride of the series. S. M. Jörgensen obtained carmine-red octahedral crystals of **chromic chloropentamminodibromide,** $[Cr(NH_3)_5Cl]Br_2$, by the action of hydrobromic acid on the chloride of the series; he also obtained a complex with mercuric bromide. R. Klement gave 2·129 for the sp. gr., and 156·2 for the mol. vol. of the dibromide. S. M. Jörgensen, and P. T. Cleve prepared **chromic chloroaquotetramminodibromide,** $[Cr(NH_3)_4(H_2O)Cl]Br_2$, by the action of hydrobromic acid on the chloride of the series. R. Werner and A. Miolati found the electrical conductivity of a mol of the salt in *v* litres of water at 25° to be :

v	125	250	500	1000	2000
μ	220·7	236·8	251·1	264·8	290·9

S. M. Jörgensen, and O. T. Christensen prepared **chromic bromopentamminodibromide,** $[Cr(NH_3)_5Br]Br_2$, by the action of hydrobromic acid on the product of the action of silver oxide on the chloropentamminodichloride. R. Klement gave 2·382 for the sp. gr., and 158·2 for the mol. vol. It forms a complex chloroplatinate. The nitrate, chloride, and chromate of the series $Cr(NH_3)_5BrX_2$ were also obtained. F. Ephraim and W. Ritter found that the salt absorbs no ammonia. A. Benrath found that the salt is stable in the presence of hydrobromic acid. R. Klement gave 1·961 for the sp. gr. and 146·9 for the mol. vol. of **chromic bromopentamminodichloride,** $[Cr(NH_3)_5Br]Cl_2$. H. Freundlich and R. Bartels studied the hydrolysis of the salt $[Cr(NH_3)_5Br]^{\cdot\cdot}+H_2O=Br'+[Cr(NH_3)_5(H_2O)]^{\cdot\cdot\cdot}$. P. T. Cleve, and P. Pfeiffer and S. Basci prepared **chromic bromoaquotetramminodibromide,** $[Cr(NH_3)_4(H_2O)Br]Br_2$, by the action of hydrobromic acid on an ammoniacal soln. of ammonium bromide and chromic hydroxide. The chloride and sulphate of the series were also prepared. A. Werner obtained **chromic bromodiaquotriamminodichloride,** $[Cr(NH_3)_3(H_2O)_2Br]Cl_2$; and also **chromic bromodiaquotriamminodibromide,** $[Cr(NH_3)_3(H_2O)_2Br]Br_2$; as well as the corresponding sulphate. P. Pfeiffer and R. Stern, and P. Pfeiffer and T. G. Lando obtained **chromic bromoaquobisethylenediaminodibromide,** $[Cr\,en_2(H_2O)Br]Br_2.H_2O$. A. Werner and J. von Halban prepared dark orange crystals of **chromic thiocyanatopentamminodibromide,** $[Cr(NH_3)_5(SCy)]Br_2$; H. I. Schlesinger and D. N. Rickles also prepared **chromium cis-dibromotetramminochloride,** $[Cr(NH_3)_4Br_2]Cl$, by the action of boiling hydrobromic acid on **chromium triamminochloroxalate,** $[Cr(NH_3)_3Cl(C_2O_4)]$. They also prepared the corresponding **chromium cis-dibromotetramminobromide,** $[Cr(NH_3)_4Br_2]Br$, **chromium cis-dibromotetramminoiodide,** $[Cr(NH_3)_4Br_2]I$, etc. They also prepared **chromium trans-dibromotetramminobromide,** $[Co(NH_3)_3Br_2]Br$, by the action of hot hydrobromic acid on chromium triamminobromide. A. Werner and J. L. Klein obtained lilac-coloured crystals of **chromic dihydroxydiaquodiamminobromide,** $[Cr(NH_3)_2(H_2O)_2(OH)_2]Br.H_2O$, by the action of pyridine on a soln. of dibromodiaquodiamminobromide; and E. Weinmann, on chromic dihydroxydiaquoethylenediaminoiodide, $[Cr(H_2O)_2\ en(OH)_2]I$. P. Pfeiffer and W. Osann prepared **chromic dihydroxydiaquodipyridinobromide,** $[CrPy_2(H_2O)_2(OH)_2]Br$. P. Pfeiffer and T. G. Lando, and A. Werner prepared **chromic cis-dichlorobisethylenediaminobromide,** $[Cr\ en_2Cl_2]Br.H_2O$, A. Werner, and P. Pfeiffer and P. Koch obtained the **trans-salt;** P. Pfeiffer and M. Tapuach, **chromic dichlorodiaquodipyridinobromide,** $[CrPy_2(H_2O)_2Cl_2]Br.3H_2O$; P. Pfeiffer and A. Trieschmann, **chromic cis-dibromobisethylenediaminobromide,** $[Cr\ en_2Br_2]Br.H_2O$, as well as the corresponding iodide, and dithionate. The **trans-salt** was also obtained as well as the corresponding iodide, nitrate, iodide, and thiocyanate. E. H. Riesenfeld and F. Seemann, and S. Guralsky prepared **chromic dibromoaquotriamminobromide,** $[Cr(NH_3)_3(H_2O)Br_2]Br$, as well as the corresponding iodide, sulphate, nitrate, and thiocyanate. Y. Shibata measured the absorption spectrum of the bromide. N. Bjerrum found that **chromic dibromotetraquochloride,** $[Cr(H_2O)_4Br_2]Cl.2H_2O$, is precipitated when a cold soln. of chromic dibromotetraquobromide in dil. hydrochloric acid is sat. with hydrogen chloride. Its constitution is deduced from its method of formation, its colour, which resembles that of the dibromobromide, and from the ease with which the halogen in the metallic complex is brought into the ionized state by soln. in water or nitric acid. He also prepared **chromic dichlorotetraquobromide,** $[Cr(H_2O)_4Cl_2]Br$, in a similar manner, as an unstable, green, crystalline powder; titration by silver nitrate shows that only one halogen atom is in the ionized state in soln. A. Werner and J. V. Dubsky, and A. Werner and J. L. Klein prepared **chromic dibromodiaquodiamminobromide,** $[Cr(NH_3)_2(H_2O)_2Br_2]Br$; and P. Pfeiffer and M. Tapuach, **chromic dibromodiaquodipyridinobromide,** $[CrPy_2(H_2O)_2Br_2]Br.4H_2O$, as well as the corresponding nitrate, and iodide. P. Pfeiffer and M. Tilgner obtained **chromic dithiocyanatotetramminobromide,** $[Cr(NH_3)_4(SCy)_2]Br$; P. Pfeiffer and P. Koch, **chromic dithiocyanatobisethylenediaminobromide,** $[Cr\ en_2(SCy)_2]Br.H_2O$, and P. Pfeiffer obtained the trans-salt; P. Pfeiffer, **chromic oxalatotetramminobromide,** $[Cr(NH_4)_4(C_2O_4)]Br.\frac{1}{2}H_2O$; H. Schwarz, P. Pfeiffer and A. Trieschmann, **chromic oxalatobisethylenediaminobromide,** $[Cr\ en_2(C_2O_4)]Br.H_2O$.

H. I. Schlesinger and D. N. Rickles prepared **chromic triamminotribromide,** $[Cr(NH_3)_3Br_3]$, **chromic triamminochlorodibromide,** $[Cr(NH_3)_3Br_2Cl]$, and **chromic triamminodichlorobromide,** $[Cr(NH_3)_3BrCl_2]$, as in the case of chromic triamminotrichloride, by the thermal decomposition of the corresponding pentammines at 175°. The corresponding iodo-, nitrato-, and nitrito-salts could not be similarly obtained.

S. M. Jörgensen, J. Petersen, and P. Pfeiffer prepared **chromium hydroxydecamminopentabromide,** $[Cr_2(OH)(NH_3)_{10}]Br_5.H_2O$, and its bromoplatinate; as well as **chromic hydroxydecamminohydroxytetrabromide,** $[Cr_2(OH)(NH_3)_{10}]Br_4(OH).H_2O$. S. M. Jörgensen described **chromic hydroxydecamminotetrabromide,** $[Cr_2(OH)(NH_3)_{10}]Br_4.2H_2O$; P. Pfeiffer and R. Stern, **chromic dihydroxybisethylenediaminotetrabromide,** $[Cr(OH)_2en_2]Br_4.2\frac{1}{2}H_2O$; S. M. Jörgensen, **chromic trihydroxyaquohexamminotribromide,** $[Cr_4(OH)_3(H_2O)(NH_3)_6]Br_3.H_2O$; P. Pfeiffer and W. Vorster, **chromic hexaquosexiesethylenediaminohexabromide,** $[Cr_4(OH)\ en_6]Br_6.4H_2O$.

A. Werner and A. Gubser prepared **rubidium chromium bromide,** $2RbBr.CrBr_3.H_2O$, or $Rb[CrBr_5(H_2O)]$, from a soln. of 3 grms. of rubidium bromide, 8 grms. of green chromic bromide, and 10 grms. of water. The brownish-violet crystals are soluble in water. S. M. Jörgensen prepared **chromic chloropentamminodibromomercuribromide,** $[Cr(NH_3)_5Cl]Br_2.2\frac{1}{4}HgBr_2$; and P. Pfeiffer, **chromic dibromobisethylenediaminobromomercuribromide,** $[Cr\ en_2Br_2]Br.HgBr_2$.

H. Rose[3] heated a mixture of potassium dichromate and bromide with sulphuric acid, and found that bromine distils over without a trace of chromium. No signs of a **chromyl bromide,** CrO_2Br_2, analogous with the corresponding chloride was obtained. S. G. Rawson also failed to prepare the compound by H. Rose's method, and also by heating calcium bromide and chromyl chloride in sealed tubes at varying temp. and varying periods of time. H. S. Fry found that a soln. of acetyl bromide in carbon tetrachloride, to which a few drops of acetic acid are added, produces an intense permanganate-red coloration, which rapidly changes to reddish-brown. The latter colour is due to bromine, and the former to an unstable chromyl bromide. The production of the permanganate-red colour is recommended as a test for traces of chromium, and is capable of detecting 0·01 mg. per 1 c.c. of solvent.

A. Ditte prepared **potassium bromochromate,** $KCrO_3Br$, from a mixed soln. of chromic acid and potassium bromide evaporated in the cold in vacuo. J. Heintze obtained it from a soln. of potassium chromate and fuming hydrobromic acid. The red crystals lose bromine in the desiccator ; water decomposes the salt into potassium dichromate and hydrobromic acid ; and with nitrogen peroxide, nitroxyl bromide is formed.

References.

[1] F. Wöhler, *Liebig's Ann.*, **111**. 383, 1859 ; M. Bauck, *Ann. Chim. Phys.*, (3), **36**. 395, 1859 ; A. J. Balard, *ib.*, (2), **32**. 337, 1826 ; *Ann. Phil.*, **12**. 381, 411, 1826 ; J. B. Berthemot, *ib.*, (2), **44**. 383, 1830 ; *Journ. Pharm. Chim.*, (2), **16**. 650, 1830 ; H. Moissan, *ib.*, (5), **25**. 408, 1882 ; *Compt. Rend.*, **92**. 1051, 1881 ; F. Bourion, *ib.*, **145**. 245, 1907 ; L. Varenne, *ib.*, **93**. 727, 1881 ; C. Löwig, *Das Brom und seine chemischen Verhältnisse*, Heidelberg, 1829 ; *Mag. Pharm.*, **23**. 11, 1828 ; **33**. 6, 1831 ; *Pogg. Ann.*, **14**. 485, 1828 ; H. Rose, *ib.*, **27**. 575, 1833 ; J. J. Berzelius, *ib.*, **1**. 34, 1824 ; A. Moberg, *Dissertatio de chloretochromoso*, Helsingfors, 1843 ; *Journ. prakt. Chem.*, (1), **29**. 175, 1843 ; E. Hein, J. Reschke and F. Pintus, *Ber.*, **60**. B, 679, 1927 ; J. M. Ordway, *Amer. Journ. Science*, (2), **26**. 197, 1858 ; C. S. Garrett, *Journ. Chem. Soc*, **103**. 1433, 1913 ; R. F. Weinland and A. Koch, *Zeit. anorg. Chem.*, **39**. 325, 1904 ; I. Koppel, *ib.*, **28**. 461, 1901 ; P. Pfeiffer, *ib.*, **24**. 286, 1900 ; *Ber.*, **34**. 2563, 1901 ; W. Biltz and E. Birk, *ib.*, **134**. 125, 1924 ; A. Werner and A. Gubser, *Liebig's Ann.*, **322**. 337, 1902 ; A. Gubser, *Ueber die Hydrate des Chromchlorids*, Zürich, 1900 ; E. Rosenbohm, *ib.*, **93**. 693, 1919 ; N. Bjerrum, *Ber.*, **40**. 2919, 3948, 1907 ; W. Traube and W. Passarge, *ib.*, **46**. 1505, 1913 ; G. O. Higley, *Journ. Amer. Chem. Soc.*, **26**. 625, 1904 ; H. S. Fry, *ib.*, **33**. 700, 1911 ; A. Recoura, *Compt. Rend.*, **110**. 1029, 1890 ; A. Byk and H. Jaffe, *Zeit. phys. Chem.*, **68**. 323, 1909 ; H. Jaffe, *Ueber die Absorptionsverhältnisse einiger Chrom- und Eisensalzlösungen im kurzwelligen Spektralgebiete*, Potsdam, 1909 ; F. Pintus, *Ueber die Existenz des einwertigen Chroms und den Einfluss der Komplexkonstitution auf die Bildung chromorganischer Verbindungen*, Leipzig, 1928.

[2] H. Freundlich and R. Bartels, *Zeit. phys. Chem.*, **101**. 177, 1922 ; S. M. Jörgensen, *Journ. prakt. Chem.*, (2), **20**. 128, 1879 ; (2), **25**. 323, 1882 ; (2), **30**. 19, 1884 ; (2), **42**. 210, 1890 ; (2), **45**. 268, 1892 ; O. T. Christensen, *ib.*, (2), **23**. 34, 1881 ; (2), **24**. 79, 1881 ; P. Pfeiffer, *Ber.*, **39**. 1873, 1906 ; **40**. 3131, 3836, 1907 ; *Zeit. anorg. Chem.*, **24**. 291, 1900 ; **29**. 136, 1901 ; **31**. 426, 1902 ; **56**. 281, 1907 ; **58**. 312, 1908 ; P. Pfeiffer and H. Pietsch, *ib.*, **58**. 308, 1908 ; P. Pfeiffer and R. Stern, *Ber.*, **40**. 3832, 1907 ; R. Stern, *Beitrag zur Chemie der Aquochromsalze*, Zürich, 1908 ; *Zeit. anorg. Chem.*, **58**. 242, 1908 ; P. Pfeiffer and M. Tilgner, *ib.*, **55**. 367, 1903 ; P. Pfeiffer and W. Vorster, *ib.*, **58**. 290, 1908 ; E. H. Riesenfeld and F. Seemann, *Ber.*, **42**. 4222, 1909 ; F. Seemann, *Ueber Chromi-aquo-Triammine*, Freiburg, 1910 ; P. Pfeiffer and R. Prade, *Zeit. anorg. Chem.*, **58**. 251, 1908 ; P. Pfeiffer and A. Trieschmann, *ib.*, **56**. 203, 1907 ; A. Trieschmann, *Beitrag zur Stereoisomerie und Koordinationsisomerie bei Chromsalzen*, Zürich, 1906 ; *Ber.*, **40**. 2837, 1907 ; P. Pfeiffer and M. Tapuach, *Ber.*, **39**. 1879, 1906 ; M. Tapuach, *Zur Kenntnis der Hydratisomerie bei Di- und Trihalogenochromsalzen*, Zürich, 1907 ; F. Ephraim and W. Ritter, *Helvetica Chim. Acta*, **11**. 848 1928 ; P. Pfeiffer and S. Basci, *Ber.*, **38**. 3596, 1905 ; S. Basci, *Beitrag zur Chemie ammoniakalischer Chromsalze*, Zürich, 1907 ; P. Pfeiffer and W. Osann, *Ber.*, **40**. 4032, 1907 ; W. Osann, *Zur Chemie der Dipyridinchromsalze*, Zürich, 1907 ; P. Koch, *Beitrag zur Stereoisomerie der Chromsalze*, Zürich, 1905 ; P. Pfeiffer and P. Koch, *Ber.*, **37**. 4273, 1904 ; P. Pfeiffer and T. G. Lando, *ib.*, **37**. 4275, 1904 ; T. G. Lando, *Beitrag zur Kenntnis der Aquo- und Diacidodiaethylendiaminchromsalze*, Zürich, 1904 ; J. Petersen, *Zeit. phys. Chem.*, **10**. 580, 1892 ; H. J. S. King, *Journ. Chem. Soc.*, **125**. 1329, 1924 ; **127**. 2100, 1925 ; S. Guralsky, *Ueber Di- und Triamminchromisalze*, Zürich, 1909 ; A. Werner, *Ber.*, **39**. 2667, 1906 ; **43**. 2286, 1910 ; **44**. 3132, 1911 ; A. Werner and J. V. Dubsky, *ib.*, **40**. 4089, 1907 ; J. V. Dubsky, *Ueber basische Salze, deren Zusammensetzung und Beziehungen*, Zürich, 1908 ; J. L. Klein, *Ueber Tetraquodiammin- und Diacidodiaquodiammin-Chromsalze*, Zürich, 1902 ; A. Werner and J. L. Klein, *Ber.*, **35**. 286, 1902 ; A. Werner and J. von Halban, *ib.*, **39**. 2670, 1906 ; *Untersuchungen über Chromammoniakverbindungen*, Zürich, 1902 ; W. Biltz and E. Birk, *Zeit. anorg. Chem.*, **134**. 125, 1924 ; A. Benrath, *ib.*, **177**. 286, 1928 ; A. Werner and A. Miolati, *Zeit. phys. Chem.*, **14**. 508, 1894 ; P. T. Cleve, *Oefvers. Akad. Förh.*, 165, 1861 ; *Svenska Akad. Handl.*, **6**. 4, 1865 ; R. Klement, *Zeit. anorg. Chem.*, **160**. 165, 1927 ; N. Bjerrum, *Ber.*, **40**. 2917, 1907 ; A. Werner and

A. Gubser, *Liebig's Ann.*, **322**. 337, 1902; A. Gubser, *Ueber die Hydrate des Chromchlorids*, Zürich, 1900; H. Schwarz, *Ueber die Beziehungen zwischen Metallammoniaken und komplexen Salzen*, Zürich, 1903; Y. Shibata, *Journ. Coll. Science Tokyo*, **41**. 6, 1919; E. Weinmann, *Diammidoverbindungen mit besonderer Rücksichtnahme auf die Tetrarhodanatodiammido-chromi-Salze*, Zürich, 1919; F. Pintus, *Ueber die Existenz des einwertigen Chroms und den Einfluss der Komplexkonstitution auf die Bildung chromorganischer Verbindungen*, Leipzig, 1928; H. I. Schlesinger and D. N. Rickles, *Journ. Amer. Chem. Soc.*, **51**. 3523, 1929; H. Farl, *Ueber die Einwirkung der Chromhaloide auf Aethyläther und über Komplexverbindungen des hierbei entstehenden Chromdihalogenäthylates*, Leipzig, 1929.

[3] H. Rose, *Pogg. Ann.*, **27**. 575, 1833; S. G. Rawson, *Chem. News*, **59**. 184, 1889; H. S. Fry, *Journ. Amer. Chem. Soc.*, **33**. 697, 1911; J. Heintze, *Journ. prakt. Chem.*, (2), **4**. 225, 1871; A. Ditte, *Compt. Rend.*, **134**. 338, 1902.

§ 27. Chromium Iodides and Oxyiodides

A. Moberg[1] observed that a soln. of chromous chloride does not give a precipitate with potassium iodide, but the soln. acquires a reddish-brown colour. H. Moissan prepared **chromous iodide**, or **chromium diiodide**, CrI_2, by heating chromic iodide in hydrogen. The greyish-white product forms a blue soln. with water; and this, on exposure, becomes green owing to the absorption of oxygen. The presence of this salt in water can induce the dissolution of the insoluble forms of the anhydrous chromic halides. W. Biltz and E. Birk gave 5·196 for the sp. gr. of **chromous hexamminodiiodide**, $CrI_2.6NH_3$.

J. Inglis observed that when a soln. of potassium dichromate is treated with an excess of conc. hydriodic acid, a dense black precipitate of iodine separates out. J. M. Ordway said that a soln. of a mol of hydrogen iodide dissolves 3 mols of chromic oxide. P. Guyot found that by heating the mixture of potassium dichromate and hydriodic acid, there remains after the expulsion of the iodine, a mixture of potassium iodide, and what was said to be **chromic iodide**, or **chromium triiodide**, CrI_3. H. Moissan obtained red crystals of anhydrous chromic iodide by the action of iodine vapour carried by a current of nitrogen over red-hot chromium; R. Hanslian observed no reaction at the b.p. of iodine. According to G. O. Higley, the violet *enneahydrate*, $CrI_3.9H_2O$, or $[Cr(H_2O)_3(H_4O_2)_3]$, is formed by passing hydrogen iodide into 30 c.c. of water in which 12·3 grms. of barium carbonate are suspended and then adding 14·5 grms. of violet chromic sulphate, and sat. the filtrate at 10° with hydrogen iodide. The dark violet or black crystals yield an olive-green powder. The salt decomposes on keeping with the evolution of hydrogen iodide; it is very hygroscopic; and it is soluble in alcohol, and in acetone, but insoluble in chloroform. W. Biltz and E. Birk gave 4·915 for the sp. gr. at 25°/4°.

S. M. Jörgensen[2] treated a soln. of chromic hexamminonitrate with a soln. of potassium iodide, and obtained **chromic hexamminotriiodide**, $[Cr(NH_3)_6]I_3$. The yellow, rhombic plates are isomorphous with the bromide. W. Biltz and E. Birk gave 2·425 for the sp. gr. at 25°/4°; and 220·6 for the mol. vol. E. Rosenbohm gave $10 \cdot 53 \times 10^{-6}$ mass units for the magnetic susceptibility. A. Benrath found that in the presence of hydriodic acid, $[Cr(NH_3)_5I]I_2$, and $[Cr(NH_3)_5(H_2O)]I_3$ are formed. P. Pfeiffer, and P. Pfeiffer and M. Tilgner prepared **chromic trisethylenediaminotriiodide**, $[Cr\ en_3]I_3.H_2O$; P. Pfeiffer and H. Pietsch, **chromic bisethylenediaminopropylenediaminotriiodide**, $[Cr\ en_2pn]I_3.2H_2O$; and P. Pfeiffer and M. Haimann, **chromic trispropylenediaminotriiodide**, $[Cr\ pn_3]I_3.H_2O$. O. T. Christensen obtained a yellow crystalline powder of **chromic aquopentamminotriiodide**, $[Cr(NH_3)_5(H_2O)]I_3$, by the action of hydriodic acid on a soln. of the corresponding hydroxide. H. J. S. King also prepared this salt.

H. J. S. King prepared **chromic hydroxypentamminodiiodide**, $[Cr(NH_3)_5(OH)]I_2.\frac{1}{2}H_2O$, as in the case of the chloride. An addition product with potassium iodide was also obtained. P. Pfeiffer and R. Stern obtained **chromic cis-hydroxyaquobisethylenediaminodiiodide**, $[Cr\ en_2(H_2O)(OH)]I_2$; and P. Pfeiffer and R. Prade, the **trans-salt.** O. T. Christensen prepared red, octahedral crystals of **chromic nitritopentamminodiiodide**, $[Cr(NH_3)_5(NO_2)]I_2$; and A. Werner and J. von Halban, **chromic**

nitratopentamminodiiodide, $[Cr(NH_3)_5(NO_3)]I_2$. S. M. Jörgensen obtained lilac plates of **chromic chloropentamminodiiodide,** $[Cr(NH_3)_5Cl]I_2$, associated with one and two mols. of mercuric iodide. P. T. Cleve prepared garnet-red, rhombic prisms of **chromic chloroaquotetramminodiiodide,** $[Cr(NH_3)_4(H_2O)Cl]I_2$. S. M. Jörgensen obtained bluish-violet, octahedral crystals of **chromic iodopentamminodiiodide,** $[Cr(NH_3)_5I]I_2$, as well as the corresponding chloride, and nitrate. H. Freundlich and R. Bartels studied the hydrolysis of the salt: $[Cr(NH_3)_5I]^{\cdot\cdot}+H_2O=I'+[Cr(NH_3)_5(H_2O)]^{\cdot\cdot\cdot}$. P. T. Cleve prepared **chromic iodoaquotetramminodiiodide,** $[Cr(NH_3)_4(H_2O)I]I_2$, in rose-red octahedra; A. Werner and J. V. Dubsky, **chromic dihydroxydiaquodiamminoiodide,** $[Cr(NH_3)_2(H_2O)_2(OH)_2]I$; E. Weinmann, **chromic dihydroxydiaquoethylenediaminoiodide,** $[Cr(H_2O)_2\,en(OH_2)]I$; P. Pfeiffer and W. Osann, **chromic dihydroxydiaquodipyridinoiodide,** $[CrPy_2(H_2O)_2(OH)_2]I$; P. Pfeiffer and T. G. Lando, P. Pfeiffer and P. Koch, and P. Pfeiffer and A. Trieschmann, **chromic cis-dichlorobisethylenediaminoiodide,** $[Cr\,en_2Cl_2]I$, and also the trans-salt; E. Rosenbohm, **chromic dichlorotetramminoiodide,** $[Cr(NH_3)_4Cl_2]I$, with the magnetic susceptibility $19{\cdot}74\times10^{-6}$ mass units; A. Werner, **chromic dichloroaquotriamminoiodide,** $[Cr(NH_3)_3(H_2O)Cl_2]I$; S. Guralsky, and A. Werner, **chromic dibromoaquotriamminoiodide,** $[Cr(NH_3)_3(H_2O)Br_2]I$; P. Pfeiffer, **chromic cis-dibromobisethylenediaminoiodide** $[Cr\,en_2Br_2]I.H_2O$, as well as the **trans-salt ;** P. Pfeiffer and M. Tapuach, **chromic dibromodiaquodipyridinoiodide,** $[CrPy_2(H_2O)_2Br_2]I.4H_2O$; P. Pfeiffer and T. G. Lando, complex salts of mercuric iodide with **chromic diiodobisethylenediaminoiodide,** $[Cr\,en_2I_2]I$; P. Pfeiffer and P. Koch, a complex salt of mercuric iodide with **chromic cis-thiocyanatobisethylenediaminoiodide,** $[Cr\,en_2(SCy)_2]I.HgI$; P. Pfeiffer and A. Trieschmann, and H. Schwarz, **chromic oxalatobisethylenediaminoiodide,** $[Cr\,en_2(C_2O_4)]I$; S. M. Jörgensen, **chromic hydroxydecamminopentaiodide,** $[Cr(OH)(NH_3)_{10}]I_5.H_2O$; F. Pintus prepared **chromic trisethylenediaminotriiodide,** $[Cr\,en_3]I_3$. S. M. Jörgensen, **chromic hydroxydecamminohydroxydichlorodiiodide,** $[Cr_2(OH)(NH_3)_{10}]Cl_2I_2(OH)$, and **chromic hydroxydecamminochlorotetraiodide,** $[Cr_2(OH)_6(NH_3)_{10}]ClI_4.H_2O$; P. Pfeiffer and R. Stern, **chromic dihydroxyquaterethylenediaminotetraiodide,** $[Cr_2(OH)_2\,en_4]I_4.2\tfrac{1}{2}H_2O$; S. M. Jörgensen, **chromic trihydroxyaquohexamminotriiodide,** $[Cr_2(OH)_3(H_2O)(NH_3)_6]I_3.H_2O$; R. F. Weinland and E. Büttner, **chromic hexacetatodihydroxytriamminoiodide** $[Cr_3(CH_3COO)_6(NH_3)_3(HO)_2]I$; R. F. Weinland and E. Gussmann, **chromic hexacetatodihydroxytripyridinoiodide,** $[Cr_3(CH_3COO)_6Py_3(OH)_2]I$; and P. Pfeiffer and W. Vorster, **chromic hexahydroxysexiesethylenediaminohexaiodide,** $[Cr_4(OH)_6en_6]I_6.H_2O$, and an addition product with mercuric iodide.

S. M. Jörgensen prepared the complex **chromic chloropentamminodiiodomercuriiodide,** $[Cr(NH_3)_5Cl]I_2.HgI$, as well as $[Cr(NH_3)_5Cl]I_2.2HgI_2$; P. Pfeiffer, **chromic diiodobisethylenediaminoiodomercuriiodide,** $[Cr\,en_2I_2]I.HgI_2$; P. Pfeiffer and P. Koch, **chromic dithiocyanatobisethylenediaminoiodomercuriiodide,** $[Cr\,en_2(SCy)_2]I.HgI_2$; and P. Pfeiffer and W. Vorster, **chromic hexahydroxysexiesethylenediaminohexaiodomercuriiodide,** $[Cr_4(OH)_6en_6]I_6.2HgI_2.8H_2O$.

As indicated above, J. Inglis,[3] and P. Guyot obtained no evidence of the formation of an oxyiodide by the action of hydriodic acid on potassium chromate. H. Giraud said that an oxyiodide is formed as a deep red, oily liquid, boiling at 149°, by the action of sulphuric acid on a mixture of potassium dichromate and iodide. H. Rose found that iodine, not **chromyl iodide,** is formed; nor could S. G. Rawson verify this, nor could he obtain an oxyiodide by the action of calcium iodide on chromyl chloride in a sealed tube; by the action of the vapour of chromyl chloride on ethyl iodide, or by the action of hydrochloric acid, acetic acid, or hydrofluosilicic acid on a mixture of potassium iodide, chromium trioxide, and solid zinc chloride. I. Walz obtained some iodate by the action of chromic acid on iodine. H. S. Fry treated chromium trioxide with acetyl iodide and obtained only iodine. There was no evidence of the formation of chromyl iodide.

According to P. Guyot, when potassium chromate is treated with colourless hydriodic acid, garnet-red crystals of **potassium iodochromate,** $KCrO_3I$, are produced. If the salt contains an excess of iodine it may have a brown tint, but on exposure to the air it gradually assumes its normal colour. It is decomposed in the presence of water into hydriodic acid and potassium dichromate. When heated it gives off iodine copiously ; on boiling it with hydriodic acid more iodine is given off, potassium iodide and chromic iodide remaining behind.

References.

[1] A. Moberg, *Dissertatio de chloretochromoso*, Helsingfors, 1843 ; *Journ. prakt. Chem.*, (1), **29**. 175, 1843 ; H. Moissan, *Compt. Rend.*, **92**. 1052, 1881 ; *Ann. Chim. Phys.*, (5), **26**. 409, 1882 ; G. O. Higley, *Journ. Amer. Chem. Soc.*, **26**. 626, 1904 ; R. Hanslian, *Molekulargewichtsbestimmungen in gefrierenden und siedenden Iod*, Weida a. Th., 1910 ; J. M. Ordway, *Amer. Journ. Science*, (2), **26**. 197, 1858 ; P. Guyot, *Compt. Rend.*, **73**. 46, 1871 ; J. Inglis, *Phil. Mag.*, (3), **7**. 441, 1835 ; (3), **8**. 12, 191 ; 1836 ; W. Biltz and E. Birk, *Zeit. anorg. Chem.*, **134**. 125, 1924.

[2] H. Freundlich and R. Bartels, *Zeit. phys. Chem.*, **101**. 177, 1922 ; S. M. Jörgensen, *Journ. prakt. Chem.*, (2), **20**. 133, 1879 ; (2), **25**. 94, 335, 1882 ; (2), **30**. 22, 1884 ; (2), **45**. 268, 1892 ; O. T. Christensen, *ib.*, (2), **23**. 37, 1881 ; (2), **24**. 81, 1881 ; E. Rosenbohm, *Zeit. phys. Chem.*, **93**. 693, 1919 ; W. Biltz and E. Birk, *Zeit. anorg. Chem.*, **134**. 125, 1924 ; A. Benrath, *ib.*, **177**. 286, 1928 ; P. Pfeiffer, *Ber.*, **34**. 4306, 1901 ; **37**. 4270, 1904 ; *Zeit. anorg. Chem.*, **24**. 293, 1900 ; **56**. 285, 1907 ; **58**. 312, 1908 ; P. Pfeiffer and M. Tilgner, *ib.*, **55**. 366, 1907 ; P. Pfeiffer and R. Stern, *ib.*, **58**. 285, 1908 ; *Ber.*, **40**. 3832, 1907 ; R. Stern, *Beitrag zur Chemie der Aquochromsalze*, Zürich, 1908 ; *Zeit. anorg. Chem.*, **58**. 242, 1908 ; P. Pfeiffer and W. Vorster, *ib.*, **58**. 293, 1908 ; P. Pfeiffer and H. Pietsch, *ib.*, **58**. 309, 1908 ; P. Pfeiffer and R. Prade, *ib.*, **58**. 255, 1908 ; M. Haimann, *Ueber Coordinationsisomerie bei Chromiaken*, Zürich, 1912 ; P. Pfeiffer and M. Haimann, *Ber.*, **36**. 1064, 1903 ; P. Pfeiffer and W. Osann, *ib.*, **40**. 4033, 1907 ; W. Osann, *Zur Chemie der Dipyridininchromsalze*, Zürich, 1907 ; P. Koch, *Beiträge zur Stereoisomerie der Chromsalze*, Zürich, 1905 ; P. Pfeiffer and P. Koch, *Ber.*, **37**. 4282, 1904 ; P. Pfeiffer and T. G. Lando, *ib.* **37**. 4280, 1904 ; T. G. Lando, *Beitrag zur Kenntnis der Aquo- und Diacido-diaethylendiaminochromsalze*, Zürich, 1904 ; A. Trieschmann, *Beitrag zur Stereoisomerie und Koordinationsisomerie bei Chromsalzen*, Zürich, 1906 ; P. Pfeiffer and A. Trieschmann, *Ber.*, **37**. 4290, 1904 ; P. Pfeiffer and M. Tapuach, *ib.*, **39**. 1879, 1906 ; A. Werner and J. von Halban, *ib.*, **39**. 2672, 1906 ; J. von Halban, *Untersuchungen über Chromammoniakverbindungen*, Zürich, 1902 ; J. V. Dubsky, *Ueber basische Salze, deren Zusammensetzung und Beziehungen*, Zürich, 1908 ; A. Werner and J. V. Dubsky, *Ber.*, **40**. 4091, 1907 ; S. Guralsky, *Ueber Di- und Triamminchromisalze*, Zürich, 1909 ; E. Weinmann, *Diammidoverbindungen mit besonderer Rücksichtnahme auf die Tetrarhodanatodiammido-chromi-Salze*, Zürich, 1919 ; P. T. Cleve, *Oefvers. Akad. Förh.*, 165, 1861 ; *Svenska Akad. Handl.*, **6**. 4, 1865 ; H. Schwarz, *Ueber die Beziehungen zwischen Metallammoniaken und komplexen Salzen*, Zürich, 1903 ; H. J. S. King, *Journ. Chem. Soc.*, **125**. 1329, 1924 ; **127**. 2100, 1925 ; A. Werner, *Ber.*, **39**. 2666, 1906 ; **43**. 2293, 1910 ; E. Büttner, *Ueber grüne und violette komplexe Chromiacetate*. Tübingen, 1912 ; R. F. Weinland and E. Büttner, *Zeit. anorg. Chem.*, **67**. 171, 1910 ; R. F. Weinland and E. Gussmann, *ib.*, **67**. 167, 1910 ; *Ber.*, **42**. 3881, 1909 ; F. Pintus, *Ueber die Existenz des einwertigen Chroms und den Einfluss der Komplexkonstitution auf die Bildung chromorganischer Verbindungen*, Leipzig, 1928.

[3] J. Inglis, *Phil. Mag.*, (3), **7**. 441, 1835 ; (3), **8**. 12, 191, 1836 ; P. Guyot, *Compt. Rend.*, **73**. 46, 1871 ; I. Walz, *Chem. News*, **29**. 245, 1872 ; S. G. Rawson, *ib.*, **59**. 184, 1889 ; H. Rose, *Pogg. Ann.*, **27**. 575, 1833 ; H. Giraud, *Phil. Mag.*, (3), **12**. 322, 1838 ; H. S. Fry, *Journ. Amer. Chem. Soc.*, **33**. 697, 1911.

§ 28. Chromium Sulphides

O. Schumann [1] made some observations on the relative affinities of chromium and the metals for sulphur and oxygen. According to A. Moberg, when chromous chloride is treated with ammonium sulphide, a black precipitate—presumably **chromous sulphide** or **chromium monosulphide,** CrS—is formed ; E. M. Péligot obtained it by the use of potassium sulphide and observed that the precipitate is insoluble in an excess of the precipitant. M. Traube observed that the sulphide occurs among the products of the reduction of chromic sulphate heated in hydrogen. H. Moissan observed that when chromous chloride is heated to 440° in hydrogen sulphide, this sulphide is formed ; this is also the case when chromic sulphide is heated in hydrogen. A. Moulot obtained this sulphide by heating chromium in an atm. of hydrogen sulphide in an electric furnace. The black mass prepared at a high temp. forms opaque, prismatic crystals of sp. gr. 4·08. The black, non-crystalline powder has a sp. gr. 3·97. W. F. de Jong and H. W. V. Willems found that the crystals of the monosulphide, prepared by heating sulphur and chromium at 600°, have an X-radiogram in agreement with a hexagonal lattice with $a=3\cdot44$ A., and $c=5\cdot67$ A.; and sp. gr. 4·85. M. Picon gave 1550° for the m.p. The crystals scratch quartz. M. Picon found that chromous sulphide is more resistant to the action of carbon at a high temp., in vacuo, than is the corresponding oxide. The sulphide melts without dissociation at 1550°. E. Wedekind and C. Horst gave $28\cdot4\times10^{-5}$ mass units for the magnetic susceptibility at 19·5°. Chromous sulphide is easily attacked by oxidizing agents, but not by reducing agents. Chromous sulphide is but slightly reduced when heated to 1200° in hydrogen; with oxygen, at a red-heat, chromic oxide and sulphate, and sulphur dioxide are formed; when heated in air, it glows, forming chromic oxide, but no sulphur is obtained; with water-vapour, chromic oxide and hydrogen sulphide are formed; with fluorine, combination occurs with incandescence, and similarly also with hydrogen fluoride; at 340°, chlorine forms chromic chloride; and carbon, in an electric furnace, forms a product free from sulphur. Molten potassium hydroxide or carbonate produces sulphate and chromate. According to M. Houdard, by heating a mixture of aluminium (7 grms.) and chromium (5·6 grms.) in a current of hydrogen sulphide, a black, crystalline mass is obtained, which evolves hydrogen sulphide with water, giving a deposit of alumina and leaving a reddish-black, crystalline residue, which, when washed with dil. hydrochloric acid, corresponds with **chromous sulphoaluminate,** $Al_2S_3.CrS$, or $Cr(AlS_2)_2$. Its optical properties resemble those of the spinels, and the crystals have the cubic structure. If excess of chromium is used, the sesquisulphide seems to be formed and the crystalline mass obtained is only with difficulty attacked by dil. hydrochloric acid, whilst nitric acid slowly destroys the double compound, leaving a black, crystalline residue of CrS. For chromous sulphochromite, *vide infra.*

H. Moissan observed that **chromic sulphide,** or **chromium hemitrisulphide,** or **chromium sesquisulphide,** Cr_2S_3, can be formed by the direct union of the elements, for chromium filings at 700° unite with sulphur vapour to form this compound; and it is also formed when hydrogen sulphide is passed over chromium at 1200°. J. J. Berzelius prepared this compound by heating an intimate mixture of sulphur and chromic oxide in vacuo; and L. R. von Fellenberg melted a mixture of chromic oxide, sulphur, and potassium carbonate. O. Harten obtained it by passing hydrogen sulphide over white-hot chromic oxide, or chromium trioxide. O. Schumann working at a lower temp. obtained only a 25 per cent. conversion. H. Moissan added that the reaction with chromic oxide, not previously calcined, sets in at about 440°. W. Müller obtained a large proportion of chromic oxide by passing hydrogen sulphide over heated potassium chromate, and extracting the potassium sulphide with water. J. L. Lassaigne heated a mixture of chromic chloride and sulphur at a red-heat, but, added J. J. Berzelius, the reaction is incomplete. J. von Liebig obtained chromic sulphide by passing hydrogen sulphide over strongly heated chromic chloride. J. J. Berzelius prepared the sulphide by melting chromic oxide and potassium pentasulphide at a high temp., and extracting the alkali sulphide with water. R. Schneider recommended preparing chromic sulphide by treating sodium sulphochromite with dil. hydrochloric acid, and heating the well-washed product in a current of carbon dioxide. F. Wöhler, and C. Brunner heated potassium chromate with potassium polysulphide, when, according to A. Schafarik, a complex alkali chromic sulphide is probably formed. K. Brückner found that when a mixture of chromic oxide and sulphur is heated in air, the oxide is not decomposed; chromium trioxide inflames and forms chromic oxide with a small proportion of sulphide; potassium chrome-alum with a prolonged heating forms chromic oxide and potassium sulphate, but if the mixture is heated for only a short period, a potassium and chromium sulphide is formed—*vide supra,* for the action of sulphur on chromates. H. Rose obtained chromic sulphide by passing the vapour of carbon disulphide over heated chromic oxide; W. Müller passed the vapour over heated potassium chromate and extracted the alkali sulphide by water; a large proportion of chromic oxide is formed if ammonium chromate is employed. E. Kopp obtained a pyrophoric mixture by reducing chromic sulphate in hydrogen; M. Traube showed that the black product is a mixture of chromic sulphide and oxide. M. Traube obtained some sulphide by heating acid chromic sulphate in dry hydrogen sulphide; A. Moulot heated the sulphate mixed with potassium polysulphide; and K. Brückner, with sulphur. H. Moissan heated chromic oxalate in hydrogen sulphide; and R. Schneider heated the higher chromium sulphides—*e.g.* $Cr_4S_7=2Cr_2S_3+S$.

Analyses of chromic sulphide in agreement with the formula Cr_3S_3 were reported by L. R. von Fellenberg, O. Harten, A. Gautier and L. Hallopeau, and A. Mourlot. A. Schafarik, W. Müller, and M. Traube obtained rather too high a proportion of sulphur. J. L. Lassaigne's analysis must have been made on a very impure sample. According to the temp. at which it has been prepared, chromic sulphide appears as a black or dark grey powder; or in bright black, or greyish-black crystals in some cases resembling graphite. A. Schafarik gave 2·79 to 3·77 for the sp. gr. of the crystals. If heated in the absence of air, H. Moissan observed that chromous sulphide is formed. M. Picon found that chromic sulphide loses sulphur at 1350°, melts at 1550°, and then has a composition $CrS_{1\cdot06}$. A. Karl said that the sulphide is triboluminescent. When the powder is used as anode in the electrolysis of 2 per cent. sulphuric acid, K. Fischbeck and E. Einecke found that as hydrogen sulphide is formed, tervalent chromium passes into soln. O. Stelling studied the X-ray spectrum. E. Wedekind and C. Horst gave $23\cdot28\times10^{-6}$ mass units for the magnetic susceptibility. M. Traube, A. Schafarik, and J. L. Lassaigne observed that chromic sulphide burns like a pyrophorus when heated in air or oxygen forming chromic oxide—W. Müller said that some green basic sulphate is formed. H. V. Regnault observed that with water vapour, hydrogen sulphide and a little chromic oxide are formed. H. Rose said that chromic sulphide is scarcely attacked by chlorine even at a high temp.; but J. J. Berzelius, H. Moissan, L. R. von Fellenberg, and O. Harten observed that the sulphide is partially decomposed by chlorine at ordinary temp., but decomposition into chromic chloride is complete at higher temp. W. Müller observed only a slight action with hydrochloric acid. J. Milbauer and E. Tucek studied the action of sulphur dioxide on the heated sulphide. According to J. J. Berzelius, some forms of chromic sulphide are decomposed by nitric acid, while other forms are attacked with difficulty. A. Schafarik observed that fuming nitric acid does not attack the sulphide in the cold, but the boiling acid readily decomposes the sulphide, and J. L. Lassaigne said that the boiling acid has very little action. H. Moissan found that nitric acid, or aqua regia attacks the sulphide with difficulty, while J. L. Lassaigne said that aqua regia converts it into chromic chloride and sulphuric acid. F. Göbel found that chromic sulphide is decomposed when heated in carbon monoxide, and carbon disulphide is formed. J. L. Lassaigne found that with fused potassium nitrate it forms potassium chromate and sulphate; but J. J. Berzelius said that it is not dissolved by soln. of potassium hydroxide or sulphide. S. M. Jörgensen treated a soln. of chromic chloropentamminodichloride with ammonium polysulphide; on adding alcohol, and allowing the turbid liquid to stand in a dark place, he obtained brick-red, rhombic plates of **chromic chloropentamminopentasulphide,** $[Cr(NH_3)_5Cl]S_5$. It is sparingly soluble in cold water, and freely soluble in hot water. It is decomposed by hydrochloric acid. S. M. Jörgensen treated chromic trihydroxyaquohexamminotrichloride with ammonium polysulphide, and obtained cinnabar-red, octahedral crystals of **chromic trihydroxyaquohexamminohemienneasulphide,** $[Cr_2(OH)_3(H_2O)(NH_3)_6]_2S_{11}.2H_2O$.

The formation of complex sulphides was studied by M. Gröger, H. Moissan, and R. Schneider. These salts can be regarded as **sulphochromites,** $M'CrS_2$, or salts of **hydrosulphochromous acid,** $HCrS_2$, or $H_2Cr_2S_4$. This acid was reported by R. Schneider to be formed as an unstable product when sodium sulphochromite is treated with dil. hydrochloric acid in the absence of air. It forms Cr_2S_4 when exposed to air; and, when heated in the absence of air, it furnishes chromic oxide and hydrogen sulphide. If potassium sulphotetrachromite, $K_2Cr_4S_7$, be similarly treated with dil. hydrochloric acid, grey crystals of **hydrosulphotetrachromous acid,** $H_2Cr_4S_7$, are formed. The crystals retain the form of the original crystals. The acid decomposes into hydrogen and chromic sulphides when heated in a current of carbon dioxide; it is unstable in air, forming water and the sulphide Cr_4S_7.

M. Gröger prepared **sodium sulphochromite,** $NaCrS_2$, by heating to redness a mixture of chromium hydroxide, sodium carbonate and sulphur (1 : 9 : 11) in a porcelain crucible until the excess of sulphur is expelled. The cold mass is extracted with water, and the residue washed with dil. soda-lye, then with alcohol, and finally with absolute alcohol. R. Schneider heated a mixture of potassium and sodium carbonates, potassium chromate, and sulphur; and F. J. Faktor, a mixture of sodium chromate and thiosulphate. E. Kunheim obtained it by heating a mixture of sodium and chromic sulphates and carbon in the electric arc. The dark red powder was found by R. Schneider to consist of dark brick-red, hexagonal plates of sp. gr. 2·55 at 15°. If heated in the absence of air it suffers no change. It is stable in air at ordinary temp., but when heated in air, it gives off sulphur dioxide forming chromic oxide and sodium sulphate. It is insoluble in water, but is decomposed by aerated water. R. Schneider obtained hydrosulphochromous acid by the action of dil. hydrochloric acid in the absence of air, and when exposed to air, Cr_2S_4 is formed. M. Gröger found that sodium sulphochromite is not attacked by conc. hydrochloric acid; cold conc. sulphuric acid is without action, but the hot acid decomposes the salt; nitric acid, and aqua regia decompose the salt forming chromic and sodium sulphates. The salt is not attacked by soln. of sodium hydroxide or sulphide.

J. J. Berzelius treated a soln. of potassium chromate with hydrogen sulphide, and obtained a dark brown liquid and chromic oxide. The liquid was thought to contain a sulphide of chromium and potassium; it deposits chromic sulphide when exposed to air, or when treated with acids; but the precipitate is decomposed by the liquid, forming, in air, potassium chromate, and sulphur. J. Milbauer obtained greyish-green crystals of **potassium sulphochromite,** $KCrS_2$, or $K_2Cr_2S_4$, by treating chromic oxide with molten potassium thiocyanate. It is stable in air, but when roasted it forms sulphur dioxide and chromic oxide; it is insoluble in water and hot hydrochloric acid, but freely soluble in aqua regia. According to R. Schneider, **potassium sulphotetrachromite,** $K_2Cr_4S_7$, is obtained by fusing potassium chromate (1 part) with potassium carbonate (24 parts) and sulphur (24 parts) for 20 minutes at a bright red-heat, allowing the mass to cool slowly, and washing it thoroughly but rapidly with cold water. It forms reddish to bluish-grey hexagonal plates with metallic lustre, and has a sp. gr.=2·77 at 15°. When four times as much chromate is used in proportion to the carbonate and sulphur, or a weight of chromium hydroxide equal to this, a grey powder is left instead of crystals; prolonged washing of this powder with hot water leaves pure chromic sulphide, Cr_2S_3, as J. J. Berzelius stated long ago. Potassium sulphotetrachromite is stable in air; it loses potassium sulphide slowly when it is washed with water; at a red-heat in a current of hydrogen, it loses one-seventh of its sulphur, leaving steel-blue crystals of **potassium sulphodichromite,** KCr_2S_3, or $K_2Cr_4S_6$, which retain the form of the sulphotetrachromite. When this compound is heated in air, it loses sulphur dioxide and leaves behind chromic oxide and potassium sulphide. Aq. soln. of potassium hydroxide or ammonia have little action; nitric acid, and aqua regia decompose it with the liberation of sulphur; hydrochloric acid, in the absence of air, forms the acid $H_2Cr_4S_7$.

M. Gröger precipitated **copper sulphochromite,** $Cu(CrS_2)_2$, from a soln. of the sodium salt by the addition of copper sulphate; R. Schneider used modifications of the process. Copper sulphochromite is not attacked by water, or hydrochloric acid; but is easily decomposed by warming with nitric acid or aqua regia. M. Gröger prepared **silver sulphochromite,** $AgCrS_2$, or $Ag_2Cr_2S_4$, as a black powder, by adding silver nitrate to a soln. of the sodium salt. R. Schneider used a modification of the process. M. Gröger could not prepare calcium, strontium, or barium sulphochromite, by an analogous process. He obtained zinc sulphochromite, $Zn(CrS_2)_2$, by heating a mixture of zinc chromate and sulphur in hydrogen; and also by treating a soln. of chromic sulphate and zinc sulphate with ammonia, and heating the dried product in hydrogen, and then admixed with sulphur. The violet-brown mass is insoluble in water and hydrochloric acid, but is decomposed by nitric acid. The corresponding **cadmium sulphochromite,** $Cd(CrS_2)_2$, was similarly prepared. M. Gröger prepared **stannous sulphochromite,** $Sn(CrS_2)_2$, by the action of stannous chloride on a soln. of the sodium salt. It is not attacked by water or hydrochloric acid, but is oxidized by nitric acid. M. Gröger, and R. Schneider obtained **lead sulphochromite,** $Pb(CrS_2)_2$, by adding lead nitrate to a soln. of sodium sulphochromite. M. Gröger heated hydrated chromic oxide with sulphur in a current of hydrogen and obtained a greyish-black powder of **chromous sulphochromite,** $Cr(CrS_2)_2$, or Cr_3S_4. It is insoluble in water, boiling hydrochloric acid, and dil. sulphuric acid, but it is soluble in nitric acid with the separation of sulphur, and the formation of chromic sulphate and nitrate. It glows when heated in air, forming sulphur dioxide and chromic oxide. E. Wedekind and C. Horst said that its sp. gr. is 3·54 at 14°; E. Wedekind and T. Veit said that it is feebly magnetic; and E. Wedekind and C. Horst gave for the magnetic susceptibility $33{\cdot}26\times10^{-6}$ mass units. M. Gröger obtained chocolate-brown **manganese sulphochromite,** $Mn(CrS_2)_2$, by heating a mixture of sulphur and manganese and chromic oxides in an atm. of hydrogen. Similarly with black **ferrous sulphochromite,** $Fe(CrS_2)_2$, which was also obtained by treating a soln. of sodium sulphochromite with a soln. of a ferrous salt. The meteoritic mineral called **daubréelite,** found by J. L. Smith in meteoritic irons, is a ferrous sulphochromite, $FeS.Cr_2S_3$, or $Fe(CrS_2)_2$. Observations were also made by F. Zambonini, and A. Brezina and E. Cohen. S. Meunier synthesized it by the action of hydrogen sulphide on a red-hot mixture of ferrous and chromic chlorides, or on a mixture of iron and chromium. By treating a soln. of sodium sulphochromite with a cobalt salt, M. Gröger prepared **cobalt sulphochromite,** $Co(CrS_2)_2$, and similarly, by using a nickel salt soln., **nickel sulphochromite,** $Ni(CrS_2)_2$.

Other chromium sulphides have been reported. M. Gröger's **chromium tritatetrasulphide,** Cr_3S_4, as indicated above, is considered to be **chromium sulphochromite.** E. Wedekind and C. Horst gave $33{\cdot}26\times10^{-6}$ for the magnetic susceptibility of Cr_3S_4 at 15·5°. As indicated above, R. Schneider obtained **chromium tetritaheptasulphide,** Cr_4S_7, as a decomposition product of $H_2Cr_4S_7$; and chromium disulphide, CrS_2, or Cr_2S_4, as a decomposition product of $H_2Cr_2S_4$. T. L. Phipson reported **chromium hemiheptasulphide,** Cr_2S_7, to be formed by passing hydrogen sulphide into a soln. of potassium dichromate sat. with ammonia, and adding hydrochloric acid to the filtrate. G. Bender was unable to confirm this result, and said that the alleged sulphide is a mixture of sulphochromite and hydrated chromic oxide.

O. Nordenskjöld reported a complex salt, **mercuric chromium trithiocyanatohexasulphodiammine,** $Cr(SCy)_3.2NH_3.6HgS$, to be formed by the action of mercuric sulphide on mercuric tetrathiocyanatodiamminochromiate.

REFERENCES.

[1] A. Moberg, *Dissertatio de chloreto chromoso*, Helsingfors, 1843; *Journ. prakt. Chem.*, (1), **29**. 175, 1843; (1), **44**. 322, 1848; J. J. Berzelius, *Oefvers. Akad. Förh.*, 204, 1844; *Pogg. Ann.*, **8**. 422, 1826; E. M. Péligot, *Compt. Rend.*, **19**. 609, 734, 1844; *Ann. Chim. Phys.*, (3), **12**. 528, 1844; H. Moissan, *ib.*, (5), **21**. 245, 1880; (5), **25**. 418, 1882; *Compt. Rend.*, **90**. 817, 1880; **92**. 1052, 1881; **119**. 189, 1894; E. Kopp, *ib.*, **18**. 1156, 1844; M. Houdard, *ib.*, **144**. 1144, 1907; S. Meunier, *ib.*, **112**. 818, 1891; M. Picon, *ib.*, **184**. 98, 1927; A. Karl, *ib.*, **146**. 1104, 1908; A. Gautier and L. Hallopeau, *ib.*, **108**. 112, 1889; A. Mourlot, *ib.*, **121**. 943, 1895; *Ann. Chim. Phys.*, (7), **17**. 543, 1899; J. L. Lassaigne, *ib.*, (2), **14**. 299, 1820; M. Picon, *Bull. Soc. Chim.*, (4), **41**. 189, 1927; *Compt. Rend.*, **189**. 96, 1929; E. Kunheim, *Ueber die Einwirkung des Lichtbogens auf Gemische von Sulfaten mit Kohle*, Berlin, 1900; F. Göbel, *Bull. Soc. Nat. Moscow*, **9**. 312, 1836; *Journ. prakt. Chem.*, (1), **6**. 386, 1835; M. Traube, *Liebig's Ann.*, **66**. 98, 1848; O. Schumann, *ib.*, **187**. 313, 1877; O. Harten, *ib.*, **37**. 349, 1841; O. Döpping, *ib.*, **46**. 172, 1843; F. Wöhler, *ib.*, **111**. 233, 1859; *Pogg. Ann.*, **11**. 148, 1827; O. Stelling, *Zeit. Physik*, **50**. 506, 1928; K. Brückner, *Monatsh.*, **27**. 52, 199, 1906; M. Gröger, *ib.*, **1**. 242, 1880; **2**. 266, 1881;

Sitzber. Akad. Wien, **81**. 534, 1880; **83**. 749, 1881; A. Schafarik, *ib.*, **47**. 256, 1863; *Journ. prakt. Chem.*, (1), **90**. 9, 1863; C. Brunner, *Mitt. Naturforsch. Ges. Bern*, 163, 1860; *Dingler's Journ.*, **159**. 356, 1861; F. Zambonini, *Riv. Min. Crist. Ital.*, **47**. 40, 1916; W. Müller, *Pogg. Ann.*, **127**. 404, 1866; L. R. von Fellenberg, *ib.*, **50**. 77, 1840; H. Rose, *ib.*, **42**. 541, 1837; J. von Liebig, *ib.*, **21**. 359, 1831; R. Schneider, *Journ. prakt. Chem.*, (2), **56**. 401, 1897; (2), **57**. 208, 1898; S. M. Jörgensen, *ib.*, (2), **20**. 136, 1879; (2), **45**. 271, 1892; T. L. Phipson, *Chem. News*, **4**. 125, 1861; G. Bender, *Ber.*, **20**. 726, 1887; E. Wedekind and C. Horst, *ib.*, **48**. 105, 1915; E. Wedekind and T. Veit, *ib.*, **41**. 3769, 1908; E. Wedekind, *Zeit. angew. Chem.*, **37**. 87, 1924; F. J. Faktor, *Pharm. Post.*, **38**. 527, 1905; W. F. de Jong and H. W. V. Willems, *Physica*, **7**. 74, 1927; J. Milbauer and J. Tucek, *Chem. Ztg.*, **50**. 323, 1926; J. Milbauer, *Zeit. anorg. Chem.*, **42**. 442, 1904; O. Nordenskjöld, *ib.*, **1**. 136, 1892; J. L. Smith, *Amer. Journ. Science*, (3), **12**. 109, 1876; (3), **16**. 270, 1878; *Compt. Rend.*, **83**. 74, 1876; **87**. 338, 1876; *Liebig's Ann.*, **194**. 304, 1878; A. Brezina, *Sitzber. Akad. Wien*, **83**. 473, 1881; A. Brezina and E. Cohen, *Die Structur und Zusammensetzung der Meteoreisen erläutert durch photographische Abbildungen geätzter Schnittflächen*, Stuttgart, 1887; K. Fischbeck and E. Einecke, *Zeit. phys. Chem.*, **130**. 21, 1927; H. V. Regnault, *Ann. Chim. Phys.*, (2), **62**. 231, 1836.

§ 29. Chromium Sulphates

E. M. Péligot[1] found that when the brown product obtained by reducing chromic chloride with potassium is treated with dil. sulphuric acid, some hydrogen is evolved, and a soln. of **chromous sulphate,** $CrSO_4$, is formed. H. Moissan treated chromium amalgam with dil. sulphuric acid; and A. Burger dissolved chromium from the aluminothermite process in sulphuric acid of sp. gr. 1·16 with the exclusion of air, at 90° to 100°, and obtained a blue soln. of chromous sulphate contaminated with some chromic sulphate. According to A. Asmanoff, an aq. soln. of chromic sulphate is reduced electrolytically at a lead cathode in an atm. of hydrogen. When reduction is complete, the chromous sulphate is precipitated by alcohol, washed with alcohol and ether, and dried in a current of hydrogen. The product is stable in dry air. H. Moissan obtained a white, crystalline powder of the *monohydrate* by treating moist chromous acetate with conc. sulphuric acid in the absence of air. This hydrate is more stable in air than is the heptahydrate; it is converted by a little water into the heptahydrate; and at a red-heat it forms chromic oxide, and sulphur dioxide and trioxide. B. Cabrera and S. P. de Rubies studied the magnetic qualities of the salt; and F. Allison and E. J. Murphy, the magneto-optic properties.

J. M. van Bemmelen observed that a sample kept for a year in a sealed tube exploded. H. Moissan obtained the *heptahydrate* by dissolving chromous acetate in dil. sulphuric acid in an atm. of carbon dioxide, and cooling the blue soln. The blue crystals are isomorphous with heptahydrated ferrous sulphate. They are soluble in water; and slightly soluble in alcohol. Conc. sulphuric acid converts the salt into the monohydrate. The aq. soln. is not wholly converted into chromic sulphate by boiling. The crystals and the blue soln. readily absorb oxygen from air, and with nitric oxide are coloured brown. According to A. Asmanoff, in presence of platinum as catalyst, the soln. oxidizes with evolution of hydrogen, the reaction being unimolecular. Sulphuric acid accelerates the reaction, but to a less extent than does hydrochloric acid. In absence of platinum, there is no measurable evolution of hydrogen with sulphuric acid present even in conc. up to $10N$, although the reaction takes place to some extent in presence of hydrochloric acid. In the latter case, the oxidation is accelerated by ammonium chloride. Very rapid oxidation takes place in ammonia soln., especially in presence of ammonium salts, which prevent the precipitation of chromous hydroxide. The reaction is then no longer unimolecular, but is autocatalyzed by the chromic ion. M. Berthelot found that the blue soln. mixed with ammonia and ammonium chloride readily absorbs acetylene and is thereby decolorized; after a short time the soln. becomes rose-red, and deposits a precipitate giving off ethylene. The acidic soln. absorbs no more acetylene than is the case with water.

According to C. Laurent, blue crystals of **ammonium chromous sulphate,** $(NH_4)_2SO_4.CrSO_4.6H_2O$, are formed by evaporating a soln. of the component salts in an atm. of carbon dioxide. The blue crystals resemble the double sulphates of the magnesium series. The salt is freely soluble in water; 100 c.c. of a sat. aq. soln. contain 55 grms. of the salt at 20°. The salt is insoluble in alcohol. It readily oxidizes in air. W. Traube and W. Passarge obtained **hydrazine chromous sulphate,** $(N_2H_4)_2H_2SO_4.CrSO_4$, by the action of hydrazine sulphate on a soln. of sulphuric acid and of chromous acetate in air-free water, covered with a layer of light petroleum as a protection from air. The precipitate is washed successively with water, alcohol and ether. C. Laurent prepared **sodium chromous sulphate,** $Na_2SO_4.CrSO_4.4H_2O$, by the action of sodium acetate on a sulphuric acid soln. of sodium sulphate. E. M. Péligot obtained rhombic prisms of **potassium chromous sulphate,** $K_2SO_4.CrSO_4.6H_2O$, by adding alcohol to a mixture of chromous chloride and a cold, sat. soln. of potassium sulphate. The crystals are isomorphous with those of potassium ferrous sulphate. C. Laurent also prepared **rubidium chromous sulphate,** $Rb_2SO_4.CrSO_4.6H_2O$; **cæsium chromous sulphate,** $Cs_2SO_4.CrSO_4.6H_2O$; **magnesium chromous sulphate,** $MgSO_4.CrSO_4.14H_2O$; **zinc chromous sulphate,** $ZnSO_4.CrSO_4.14H_2O$; as well as complexes of manganese and ferrous sulphates (*q.v.*).

The anhydrous **chromic sulphate,** $Cr_2(SO_4)_3$, reported by A. Schrötter[2] to be formed by heating a basic sulphate with conc. sulphuric acid until the acid begins to fume was supposed, by M. Traube, L. and P. Wöhler and W. Plüddemann, and M. Siewert, to be the acid salt. T. Klobb, however, obtained the red sulphate of the composition, $Cr_2(SO_4)_3$, by heating ammonium chromic sulphate with boiling, conc. sulphuric acid. A. Schrötter, and M. Siewert obtained it by heating the hydrated salt over 280° in a current of carbon dioxide. M. Siewert's, and T. Klobb's analyses agreed with the formula $Cr_2(SO_4)_3$; and A. Recoura gave the formula $Cr_2(SO_4)_6Cr_2$ in agreement with that for $Cr_2(SO_4)_6Fe_2$. The powder is rose-coloured in daylight, and green by gas-light. P. A. Favre and C. A. Valson gave 2·743 for the sp. gr. at 17·2°; A. Sénéchal, 2·221 at 30°; E. Moles and M. Crespi, 3·712 at 25°/4°; while L. F. Nilson and O. Pettersson gave 3·012 for the sp. gr.; 130·27 for the mol. vol.; 0·1718 for the sp. ht.; and 67·41 for the mol. ht. K. Friedrich found that the thermal decomposition curve is somewhat complex; the gases, sulphur dioxide and trioxide and oxygen, have one atm. press. at 750°. R. Robl observed but a faint luminescence in ultra-violet light. E. Kunheim studied the decomposition of mixtures of chromic sulphate and carbon in the electric arc.

According to A. Schrötter, crystals of the **violet hydrate,** which is provisionally taken to be the *octodecahydrate*, $Cr_2(SO_4)_3.18H_2O$, are obtained by allowing to stand for a few weeks a soln. of hydrated chromic oxide in the calculated quantity of conc. sulphuric acid. The soln. in water is dark blue by reflected light, and ruby-red by transmitted light; alcohol precipitates from the soln. a pale violet, crystalline powder and the soln. becomes colourless—only when there is an excess or a deficiency of acid does the soln. remain green. To obtain good crystals, he recommended dissolving the crystalline powder in a moderate quantity of water, adding dil. alcohol to the stage at which precipitation begins, and leaving the soln. to evaporate spontaneously in a vessel covered by a bladder. H. Löwel dissolved 50 grms. of dried hydrated chromic oxide in 125 grms. of conc. nitric acid; added 125 c.c. of water, and boiled for 15 min. When the liquid was cold, he added a cold soln. of 75 grms. of conc. sulphuric acid in 150 grms. of water, followed by 1200 grms. of alcohol. The precipitated crystalline powder was washed with alcohol, and dried between bibulous paper. H. Baubigny used a similar process. M. Traube allowed alcohol to drop into a soln. of chromium trioxide, conc. sulphuric acid, and water (1 : 1·5 : 3); at the end of the reduction, the chromic sulphate is precipitated by alcohol. If the temp. rises during the reduction, the green sulphate is formed. This can be converted to the violet form by boiling the liquid with nitric acid. T. W. Richards and F. Bonnet, and M. A. Graham used this process. M. Traube also obtained the violet sulphate by passing a mixture of chromic acid, conc. sulphuric acid, and water (1 : 1·5 : 2·25) into a wide basin in which a porcelain crucible containing ether is placed. Crystals of the sulphate are formed in a few hours. To complete the reduction, a few drops of alcohol may be added. G. O. Higley prepared this salt by adding 100 grms. of chrome-alum to a cold soln. of 100 c.c. of conc. sulphuric acid, and 330 c.c. of water; and pouring 260 c.c. of conc. sulphuric acid, with constant stirring, into the filtered soln. at 15° to 20°. Hydrochloric acid can be used as solvent for the alum. R. F. Weinland and R. Krebs obtained good crystals from a soln. of a mol of alum in 60 to 80 mols of H_2SO_4 in 95 per cent. soln. by cooling and evaporation in a vacuum desiccator; they also obtained the salt by adding alcohol to a soln. of chromium chlorosulphate; F. Krauss and co-workers used a similar process. A. Werner and A. Gubser obtained the salt by adding sulphuric acid to a violet soln. of chromic chloride; and P. M. Strong, by treating the mother-liquor from the preparation of the polychromosulphuric acid with the necessary quantity of green sulphate and sulphuric acid, concentrating the mixture on a water-bath; and allowing it to stand in the cold for 3 or 4 days to crystallize. E. Wydler also described the preparation of the salt.

There are differences of opinion about the water of crystallization. Analyses by G. O. Higley, A. Werner and A. Gubser, A. Étard, and M. Siewert correspond with the *hexadecahydrate*, $Cr_2(SO_4)_3.16H_2O$, for the air-dried salt; and by A. Sénéchal, with the *tetradecahydrate*, $14H_2O$. A. Schrötter said that the pentadecahydrate, $Cr_2(SO_4)_3.15H_2O$, is formed when the salt is dried at 35°. R. F. Weinland and R. Krebs obtained with all modes of preparation tried, needles and plates of the *heptadecahydrate*, $Cr_2(SO_4)_3.17H_2O$. A. Sénéchal obtained with the preparations with precipitated alcohol, $Cr_2(SO_4)_3.16{\cdot}0$ to $17{\cdot}5H_2O$, and after exposure to dry air, $Cr_2(SO_4)_3.14H_2O$; he also gave for the vap. press., p mm. of differently hydrated salts, $Cr_2(SO_4)_3.nH_2O$:

n		17·25	16·55	15·77	15·05	14·78
	25·6°	20·1	—	11·0	11·1	—
	29·3°	24·4	17·4	14·0	13·8	12·8
p at	34·0°	31·5	24·2	19·1	18·4	17·3
	38·5°	39·1	31·9	24·9	23·5	—
	40·4°	43·4	—	27·7	26·2	—

From these results, A. Sénéchal concluded that hydrates with $17H_2O$, $16H_2O$, $15H_2O$, and $14H_2O$ are chemical individuals, and that the tetradecahydrate slowly loses water at room temp. and has, at 29·3°, a vap. press. of 3 mm. M. Siewert said that when the salt was dried for an hour in the sun, it contained $12H_2O$; G. D. van Cleeff, that when the octodecahydrate is dried over sulphuric acid, it loses 3·5 to $4{\cdot}0H_2O$, at 75° it changes colour, with the loss of more water, and at 100°, it retains $4H_2O$; A. Schrötter, that the salt dried at 100° has 5 to $6H_2O$; A. Recoura, that at 90°, it forms the green hydrate with $8H_2O$; A. Kling and co-workers said $5H_2O$; and A. Étard, A. Schrötter, and A. Colson added that at 100°, the salt melts in its water of crystallization and retains $6H_2O$ and solidifies into a green gummy mass. G. N. Wyrouboff found that when dried at 110°, the salt retains $5H_2O$, and it loses no more water even when heated to 150°. M. Siewert stated that at 280°, in a current of carbon dioxide, most of the water is driven off, and all is expelled below a red-heat. G. T. Gerlach made some observations on this subject; and for those of A. Sénéchal—*vide infra*. According to W. R. Whitney, and A. Sénéchal, all products with less than $12H_2O$ are not to be considered as hydrates of the violet sulphate. G. N. Wyrouboff represented the violet sulphate by the formula $Cr_2(OH_2)_4(OH_2)_2(SO_2)_3(OH_2)_6$; and W. R. Whitney represented it by the formula $[Cr_2(H_2O)_{12}](SO_4)_36H_2O$, or $[Cr(H_2O)_6]_2(SO_4)_3.6H_2O$, which is taken best to represent the properties of the salt in aq. soln. and in the solid state. E. Moles and M. Crespi found that $[Cr(H_2O)_6]_2(SO_4)_3.5H_2O$ lost 3 mols. of water at 18°; and $[Cr(H_2O)_6]_2(SO_4)_3.2H_2O$ lost 10·7 mols. of water at 140°. According to F. Krauss and co-workers, the octodecahydrate furnishes the *enneahydrate*, $Cr_2(SO_4)_3.9H_2O$, which is stable between 30° and 100°, but the *trihydrate*, $Cr_2(SO_4).3H_2O$, has only a small range of existence. The three mols. of water are combined as in the zeolites and are therefore given up slowly. Complete dehydration occurs at about 325°.

According to A. Schrötter, and R. F. Weinland and R. Krebs, the violet hydrate forms octahedral crystals belonging to the cubic system. A. Schrötter gave 1·696 for the sp. gr. at 22°; and P. A. Favre and C. A. Valson, 1·867 at 15°. E. Moles and M. Crespi found the sp. gr. of $[Cr(H_2O)_6]_2(SO_4)_3.5H_2O$ to be 1·840 at 25°/4°, and the mol. vol. 375 to 379; and of $[Cr(H_2O)_6]_2(SO_4)_3.2H_2O$, 1·976 for the sp. gr. at 25°/4°, and 326 for the mol. vol. A. Schrötter observed that the violet salt is freely soluble in water; the percentage solubility is 54·65 per cent., but by analogy with violet hydrated chromic chloride, the solubility must depend on the equilibrium: violet sulphate$\rightleftharpoons$green sulphate. F. Krauss and co-workers observed that the dehydration curve showed breaks corresponding with 18-, 9-, 3-, and 0-hydrates. E. N. Gapon discussed some relationships of the m.p. P. A. Favre and C. A. Valson gave −3·255 Cals. for the heat of soln. per mol of $Cr_2(SO_4)_3.15H_2O$; and A. Recoura, −6·2 Cals. for a mol of $Cr_2(SO_4)_3.16H_2O$. The difference in the results may be due to differences in the proportions of the green and violet hydrates formed in different methods of preparation, etc. A. Sénéchal's results are in agreement with those of A. Recoura, for he found for the heat of soln. at 14° of the tetradecahydrate, −10·10 Cals.; for the pentadecahydrate, 8·3 Cals.; for the hexadecahydrate, −7·49 Cals.; and for the heptadecahydrate, 6·35 Cals. T. Dreisch studied the ultra-red absorption spectrum of soln. of chromic sulphate. E. Feytis said that there is no difference between the magnetic susceptibilities of the different hydrates, for the coeff. of magnetization are in all cases round about 1400×10^{-6}. G. Jäger and S. Meyer gave 31×10^{-6} mass units for the magnetic susceptibility of the soln. at 18°; and O. Liebknecht and A. P. Wills, 15×10^{-6} mass units at the same temp. V. N. Ipatieff and B. A. Mouromtseff found that soln. of chromic chloride are reduced by hydrogen under a press. of 200 atm. A. Mailfert studied the action of ozone. K. H. Butler and D. McIntosh found that the sulphate is insoluble in liquid chlorine and has no effect on the b.p. of the liquid. The violet crystals, said M. Traube, can be boiled with alcohol at 80° without passing into the green salt; on the other hand, A. Schrötter said that if a layer of alcohol be poured over the violet soln. contained in a narrow glass vessel, so as not to mix the liquids, the aq. soln. acquires a green colour starting from above and working downwards. This is attributed to the alcohol attracting or withdrawing water from the violet salt so as to form the green salt. According to A. Étard, cold monohydrated nitric acid, sulphuric acid, and phosphorus trichloride abstract water from the violet solid or soln. forming the green salt. The actual cause of the colour change is not certain. K. Schorlemmer investigated the oxidation of chromic salts to chromates by hydrogen dioxide. A. Violi found that molten sulphur converts the sulphate into chromic sulphide and sulphur dioxide. According to A. Recoura, complexes in which acetic anhydride replaces some of the water of hydrated salts are called *acetylated salts*; such an association, $Cr_2(SO_4)_3.4H_2O.4(C_2H_3O)_2O$, is formed by the slow action of finely powdered hydrated chromic sulphate on acetic anhydride.

According to A. Recoura, the **green hydrate,** which he regarded as the *henahydrate*, $Cr_2(SO_4)_3.11H_2O$, is obtained by reducing chromic acid in the presence of sulphuric acid, say, by pouring 40 c.c. of conc. sulphuric acid, and 35 c.c. of 95 per cent. alcohol into a mush of 50 grms. of chromium trioxide and 13 grms. of water. The product is dried in vacuo. A. Recoura obtained what he regarded as the *octohydrate*, $Cr_2(SO_4)_3.8H_2O$, by heating the violet sulphate to 100°. A. Étard, and A. Colson said that the product is a *hexahydrate*, and G. N. Wyrouboff, a *pentahydrate*. According to A. Sénéchal, the air-dried violet hydrate, $Cr_2(SO_4)_3.14H_2O$, begins to turn green in vacuo at 30°, and in air at 55° with the simultaneous loss of water. If the product be dissolved in water, and the violet sulphate crystallized out by cooling the soln. with ice-water, there remains, on evaporating the soln. to dryness, hexahydrated $Cr_2(SO_4)_3.6H_2O$, or $[Cr_2(SO_4)_3(H_2O)_6]$. This loses water at

80°, forming the trihydrate, $Cr_2(SO_4)_3.3H_2O$, or $[Cr_2(SO_4)_3(H_2O)_3]$, and at the same time its solubility is reduced. The trihydrate loses water at 150°, forming a greyish-green and then a greyish-red product which is insoluble in water, and loses all its water at 400°. The mol. vols. of the sulphates with 3 to 14 mols. of water are additive; but not so with those containing less water. E. Moles and M. Crespi gave 2·429 for the sp. gr. of $Cr_2(SO_4.H_2O)_3$ at 25°/4°, and 145 for the mol. vol. They also found that it lost 3·01 mols. of water at 350°. F. Krauss and co-workers showed that the dehydration curve of the green hydrate is the *dodecahydrate*, $Cr_2(SO_4)_3.12H_2O$, and when heated, 2 mols. of water behave like zeolitic water; then the hexahydrate, $Cr_2(SO_4)_3.6H_2O$, is formed; and finally, at about 400°, the anhydrous green chromate is formed. All the water in the green, amorphous *pentadecahydrate*, $Cr_2(SO_4)_3.15H_2O$, is zeolitic, and is all lost at 400° and 100 mm. Barium chloride precipitates all the SO_4 from a cold soln. of the violet sulphate, but not completely from a warm soln.; the green soln. of the dodecahydrate gives up most of the SO_4 to barium chloride, and all is given up at 100°. The cold soln. of the green, amorphous pentadecahydrate gives no precipitate with barium chloride, but if the soln. be aged, or boiled for some time, sulphate is precipitated.

According to A. Recoura, the hygroscopic green sulphate is stable, but the green aq. soln. gradually becomes violet. A freshly prepared soln. is precipitated neither by a barium salt nor by sodium hydrophosphate so that it behaves neither like a sulphate nor like a chromium salt. Alkali hydroxides precipitate from the soln. a basic salt with only two sulphate-radicles, namely, $Cr_2O(SO_4)_2$; and the heat of formation is $Cr_2O_{3aq.}+2H_2SO_4=Cr_2O_3.2SO_{3aq.}$; and $Cr_2O(SO_4)_{2aq.}+H_2SO_4=-0{\cdot}2$ Cal. The heat of transformation from the dissolved violet to the green salt is $-23{\cdot}15$ Cals., showing that the stable form is the violet salt. The isomerism between the green and violet sulphates is analogous to that between the green and violet chlorides or bromides. According to H. G. Denham, the green sulphate has twice the mol. wt. of the violet salt, and its formula is taken to be $[Cr_4(SO_4)_4](SO_4)_2$. It is strongly hydrolyzed in aq. soln. forming, in conc. soln., $[Cr_4(SO_4)_4](SO_4)(OH)_2$, and in dil. soln., $[Cr_4(SO_4)_4](OH)_4$. The transformation from the violet to the green sulphate is represented: $2Cr_2(SO_4)_3=[Cr_4(SO_4)_4](SO_4)_2$.

The basic or *modified sulphate* is a different case. Its soln. is obtained from the violet salt when heated, but it has not been obtained in the crystalline state—it furnishes a viscid syrup. The modified soln. is obtained by heating the violet soln. for a long time at 100°, and then cooling it rapidly. In the modified sulphate one-third of the sulphate can be precipitated by barium chloride. It is thought to be a complex base, $[Cr_4O(SO_4)_4](OH)_2$. A. Colson said that by heating a soln. of the violet salt, $Cr_2(SO_4)_3$, it is transformed into a pentasulphate, $HSO_4(CrSO_4)_2{-}O{-}(CrSO_4)_2.OH$, in which four of the SO_4-radicles are masked; if the boiling be continued a further hydrolysis occurs, and $SO_4Cr.O.O.Cr(SO_4)_2.O.CrSO_4$ is formed.

A. Colson said that there are three types of the green sulphate. These differ in their behaviour towards soln. of barium chloride, in their heats of formation, and in their sp. gr. The first type has *all three SO_4-radicles completely masked*, meaning that a soln. of a salt gives no precipitate with barium chloride. It is formed by the action of sulphur dioxide on a 5 per cent. soln. of chromic acid cooled by a freezing mixture; and also by evaporating a soln. of the green salt in sulphuric acid, extracting the unchanged violet salt by alcohol at 75°, and evaporating the liquid in vacuo. The green, hygroscopic, transparent plates, $Cr_2(SO_4)_3.6H_2O$, are soluble in alcohol at 75° but insoluble at 92°; the heat of formation is 33 cals.; and when the soln. has stood for about 3 days, it passes into a soln. of the second type in which two of the *three SO_4-radicles are masked*, meaning that barium chloride precipitates from the aq. soln. only one-third of the contained sulphate. B. Cabrera and S. P. de Rubies found that the electrical conductivity and unmasking of the SO_4-radicles of a soln. of the salt increase in a parallel way on keeping; no appreciable change in magnetic susceptibility occurs. The evaporation of the aged soln. in vacuo gives a salt, $Cr(SO_4)_3.8H_2O$, resembling that with three masked SO_4-

radicles. It loses water over phosphorus pentoxide in vacuo, and then consists of $Cr_2(SO_4)_3.7\frac{1}{2}H_2O$. Its heat of formation is 36·6 Cals. An isomeric form with two masked SO_4-radicles is said to be obtained by heating the violet sulphate to 90° and keeping the residue in water for 3 or 4 days below 5°. The two forms are said to differ in their heats of reaction with barium chloride, and in the electrical conductivity of their soln. In the third type *one only of the three SO_4-radicles is masked*, for, when the aq. soln. is treated with barium chloride, two-thirds of the contained sulphate is precipitated. This salt, $Cr_2(SO_4)_3.7\frac{1}{2}H_2O$, is prepared by the long-continued action of water on either of the two former types; or by precipitating hydrated chromic oxide from either soln., dissolving the product in sulphuric acid, and evaporating the soln. in vacuo. The heat of formation is 43·5 Cals.

It will be observed that the second and third types are formed by the progressive hydrolysis of the first type, and that there is simultaneously a change in the sp. gr., f.p., conductivity, and other properties of the soln. It is therefore assumed that the first type is to be regarded as $Cr_2(SO_4)_3.nH_2O$, or $[Cr_2(SO_4)_3].nH_2O$; the second, as $Cr_2(SO_4)_3(H_2O).nH_2O$, or $[Cr_2(H_2O)(SO_4)_2]SO_4.nH_2O$; and the third, as $Cr_2(SO_4)_3(H_2O)_2.nH_2O$, or $[Cr_2(H_2O)_2SO_4](SO_4)_2.nH_2O$; while the violet sulphate which has *no masked SO_4-radicles* is considered to be $Cr_2(SO_4)_3(H_2O)_3.nH_2O$, or $[Cr_2(H_2O)_3](SO_4)_3.nH_2O$. Each mol. of constitutional water is said to unmask one SO_4-radicle. According to the co-ordination theory, these four sulphates can be represented:

$$\begin{array}{cc} [Cr_2(H_2O)_{12}](SO_4)_3 & \underbrace{\begin{array}{ccc} [Cr_2(H_2O)_{10}(SO_4)](SO_4)_2 & [Cr_2(H_2O)_8(SO_4)_2]SO_4 & [Cr_2(H_2O)_6(SO_4)_3] \\ \tfrac{1}{3}SO_4\text{-masked.} & \tfrac{2}{3}SO_4\text{-masked.} & \text{All } SO_4\text{-masked.} \end{array}}_{\text{Green sulphate.}} \\ \text{Violet sulphate.} & \end{array}$$

It is of course possible that intermediate products are formed. A. Colson supposed that a cold soln. of chromic sulphate is an equilibrium mixture of the violet sulphate and three green sulphates: $Cr_2(SO_4)_3.6H_2O$, $Cr_2(SO_4)_2(OH)(HSO_4)$, and $Cr_2(SO_4)(OH)_2(HSO_4)_2$. Whatever be the nature of the complex salts existing in soln., a state of equilibrium is ultimately attained and this is dependent on the concentration and temp. of the liquid. T. W. Richards and F. Bonnet showed that the reactions which occur are reversible, for if $0·25N$-soln. of the green and violet salts are kept for a month at 30°, the amount of acid present, as indicated by the effect of the soln. on the inversion of cane-sugar, is the same in both cases, and approximates $0·043N$. At 50°, the acid so produced approximates to about $0·10N$, and at 100°, to $0·13N$. This shows that the hydrolytic equilibrium varies with the temp. The kinetics of the reactions have not been closely investigated, but some observations by A. Colson showed that the reactions are very slow at ordinary temp.; they are faster with warmer soln., and at 100°, the transformation into the modified salt occupies a few minutes. A. Kling and co-workers measured the variation with time of the amount of sulphuric acid in the soln. precipitable by benzidine hydrochloride, the lowering of the f.p. and the electrical conductivity of $0·5N$-green $Cr_2(SO_4)_4$. It was found that during the first twenty-four hours after the preparation of the soln. no sulphate precipitate is obtainable, but after that time the amount increases at first rapidly, and then gradually with passage of time. The mol. lowering of the f.p. and the electrical conductivity at first increase rapidly, even before the presence of the SO_4''-ion can be detected, and then attain a value which remains almost constant during the rest of the experiment. The green soln. of chromium sulphate tend towards a state of equilibrium, which is a function of the temp. and conc., and is the state towards which the violet soln. of the same conc. gradually pass. The properties of the chromium sulphate liquors with respect to their masked sulphate groups were studied by W. Schindler and K. Klanfer, E. Stiasny and co-workers, R. Reinicke, H. B. Merrill and co-workers, and G. Grasser.

By cooling conc. soln. of the violet salt crystals of that salt can be readily obtained, but with soln. of the green salt, or of the so-called modified salt, only gummy or glassy masses are obtained. A. W. F. Sprung found the sp. gr. of a 24 per cent. soln. of the violet salt to be 1·1619, when that of the modified salt is 1·1486; and P. A. Favre and C. A. Valson gave 1·0600 for a N-soln. of the violet salt at 15°; and 1·0556 with the modified salt at 14·9°. G. T. Gerlach found the sp. gr. of green soln. to be greater than those of violet soln.; and he gave for the sp. gr. at 15°/15° of violet soln. with the following percentage proportions of $Cr_2(SO_4)_3$:

$Cr_2(SO_4)_3$.		2·74	5·48	10·96	16·44	21·92	27·40	38·36	43·84
Sp. gr.	Green	1·0275	1·0560	1·1150	1·1785	1·2480	1·3250	—	—
	Violet	—	1·0510	1·1070	1·1680	1·2340	1·3055	1·4650	1·5530

According to A. Colson, an expansion occurs when a soln. of the violet salt passes into a soln. of the modified salt, and conversely the sp. gr. of a soln. of the green salt is intermediate between those of a soln. of the violet and of the modified salt. M. A. Graham found for the sp. gr. of soln. containing the following proportions of $Cr_2(SO_4)_3$ per litre:

$Cr_2(SO_4)_3$.	0°	10°	20°	30°	40°	50°
40·14 . .	1·0394	1·0391	1·0369	1·0342	1·0292	1·0242
63·39 . .	1·0617	1·0602	1·0585	1·0585	1·0512	1·0462
83·77 . .	—	—	1·0763	1·0763	1·0680	1·0628
126·30 . .	—	—	1·1160	1·1160	1·1062	1·1002

The soln. develop a green colour at 40° and 50° so that the solute is doubtless a mixture of the green and violet salts. A. W. F. Sprung found that the viscosity of the violet soln. is much greater than is the case with eq. soln. of the modified salt; M. A. Graham obtained the following values for the viscosities of soln. containing the indicated number of grams of $Cr_2(SO_4)_3$ per litre:

$Cr_2(SO_4)_3$.	10°	20°	25°	30°	40°	50°
19·64 . .	0·01577	0·01198	0·01062	0·00955	0·00776	0·00640
40·14 . .	—	0·01200	0·01065	0·00953	0·00774	0·00643
63·39 . .	0·01815	0·01355	0·01202	0·01076	0·00874	0·00787
83·77 . .	0·02028	0·01539	0·01396	0·01206	0·06975	0·00795
126·30 . .	0·02705	0·02072	0·01827	0·01621	0·01301	0·01041

The same remarks apply to these results as to those given with respect to the sp. gr. at 40° and 50°. G. D. van Cleeff observed that in the dialysis of soln. of the salt the dialyzed part contains more acid than the part which remains; this was confirmed by M. D. Dougal, and T. W. Richards and F. Bonnet found that when a violet soln. of chromium sulphate is subjected to dialysis, the ratio Cr/SO_4 of the salt that has diffused and the salt that has remained in the dialyzer is the same in both. When, however, a green soln. of chromium is similarly treated, the ratio Cr/SO_4 diminishes in the diffused portion and increases in the dialyzer—an observation in favour of the view that the change from violet to green involves a hydrolysis with formation of free acid and a soluble basic salt.

The lowerings of the f.p. of violet soln. of the sulphate have been measured by A. Colson, H. G. Denham, and H. C. Jones and E. Mackay. The last-named found that for soln. with 0·025, 0·050, 0·10, and 0·250 mol per litre, the f.p. was —0·121°, —0·230°, —0·417°, and —1·029°. The results indicate that for the most dil. soln., five ions per mol. are formed. For 0·083N-soln. of the modified sulphate, H. G. Denham gave —0·420° for the f.p. of the modified soln., and A. Colson, for very rapidly cooled modified 0·1N- and 0·2N-soln., respectively —0·45° and —0·85°. H. G. Denham also measured the f.p. of sulphuric acid soln. The results show that the f.p. of the modified soln. is less than that of the violet soln., and if the hydrolysis of the salt is hindered by the presence of sulphuric acid, the apparent mol. wt. of the modified sulphate is greater than that of the violet salt. T. W. Richards and F. Bonnet, and M. A. Graham examined the f.p. of mixed soln. of chromium sulphate and cane-sugar. H. G. Denham observed that the f.p. of soln. of $\frac{1}{12}N$-soln. of violet and modified sulphate sat. with hydrated chromic oxide are respectively

—0·335° and —0·268°. The results are taken to show the existence of a complex Cr_4-cation is formed, but migration experiments do not agree with the view that the complexity is due to the presence of such a complex. A. Colson found that soln. freshly prepared in the cold from the solid green sulphate show a small depression of the f.p. which rapidly rises until a value corresponding with that required for the violet soln. is attained. K. Flick studied the thermal decomposition of solid chromic sulphate.

According to A. Recoura, the heat of transformation of a mol of the dissolved green sulphate into the modified sulphate is 4·2 Cals., and into the violet sulphate, 23·15 Cals., so that the heat of transformation of a mol of the modified to the violet sulphate in soln., is 18·95 Cals. per mol. When a mol of dissolved sodium hydroxide is added to a mol of chromic sulphate in 12 litres of a modified soln., 15·61 Cals. are developed, while the addition of more sodium hydroxide develops only a little more heat; a mol of sodium hydroxide neutralizes only one-sixth of the sulphuric acid, and $\frac{1}{2}H_2SO_4$ in 12 litres of soln. with a mol of NaOH in 2 litres develops 15·63 Cals., it follows that about one-sixth the sulphuric acid was present in the soln. as free acid. A. Colson came to the same conclusion because he found that a mol of $Cr_2(SO_4)_3$ in modified soln. with $\frac{1}{2}Ba(OH)_2$ develops 18·7 Cals., while $\frac{1}{2}H_2SO_4 + \frac{1}{2}Ba(OH)_2$ develops 18·5 Cals. A mol of chromic sulphate in a green soln. with no precipitable SO_4, with 6 mols of potassium hydroxide develops 61·05 Cals., so that the heat of neutralization of the precipitated hydroxide with $3H_2SO_4$ is 33·12 Cals.; a similar soln. with one-third precipitable SO_4 develops with 6KOH, 57·6 Cals., and the heat of neutralization of the precipitated hydroxide with sulphuric acid is 36·6 Cals. Likewise with a mol of chromic sulphate with two-thirds precipitable SO_4 and 6KOH develops 43·5 Cals. With the violet soln. where all the SO_4 is precipitable, each SO_4 develops 6·65 Cals., for $H_2SO_4 + BaCl_2 = BaSO_4 + 2HCl + 9{\cdot}5$ Cals. Otherwise expressed, with a mol of $Cr_2(SO_4)_3$ in modified soln., the addition of $\frac{1}{2}$ a mol of $BaCl_2$ develops 7·20 Cals. per mol of $BaCl_2$, and with another $\frac{1}{2}$ mol of $BaCl_2$, 7·06 Cals. per mol of $BaCl_2$; and with yet another $\frac{1}{2}$ mol of $BaCl_2$, 0·15 Cal. Accordingly, only one-third of the total sulphate reacts with barium chloride. Using a mol of $Cr_2(SO_4)_3$ in an aged green soln., the addition of one mol of $BaCl_2$ develops 7·1 Cals.; 2 mols, 14·1 Cals.; and 3 mols, 14·7 Cals. This shows that two-thirds of the total SO_4 is precipitated. According to A. Kling and coworkers, a fresh soln. of a mol of chromic sulphate, in ice-cold water, exhibits no thermal change.

L. R. Ingersoll found for Verdet's constant for the electro-magnetic rotatory power for light of wave-length 0·8, 1·0, and 1·25μ, respectively 0·0067, 0·0045, and 0·0028 for soln. of chromic sulphate of sp. gr. 1·140. The absorption spectra of violet and green soln. of chromic sulphate were examined by D. Brewster, H. F. Talbot, W. N. Hartley, J. M. Hiebendaal, O. Knoblauch, W. Böhlendorff, A. Étard, G. Massol and A. Faucon, Y. Shibata and H. M. Vernon. H. C. Jones, and W. W. Strong found that with soln. of the violet sulphate at 5°, the three characteristic chromium bands appear—*viz.*, the ultra-violet band extending to $\lambda=2800$; the bluish-violet band from $\lambda=4100$ to 4450; and the yellowish-green band from $\lambda=5500$ to $\lambda=6200$. The bands at $\lambda=6800$ are very faint. The absorption in the visible spectrum is very strong. At 82°, the ultra-violet band extends to $\lambda=2900$, the bluish-violet band from $\lambda=4100$ to 4550, and the yellowish-green band from $\lambda=5500$ to 6300. The effect of a rise of temp. is therefore very small, usually involving a shifting of the long wave-length edges of all three bands towards the red. M. A. Graham found that the ultra-violet absorption spectra of green and violet soln. indicate that the change in colour which occurs is not due to simple hydrolysis, but is the result of a process involving both hydrolysis and a change in structure. T. Svensson found that the electrical conductivity of soln. of chromic sulphate slowly decreases in light.

The mol. electrical conductivity of the violet soln. has been determined by P. Walden, W. R. Whitney, A. Gubser, M. A. Graham, A. Colson, and H. C. Jones and E. Mackay. L. G. Winston and H. C. Jones observed for violet soln., the mol. conductivity, μ mhos, for soln. of a mol of the salt in v litres, and α, the percentage ionization,

	v . .	4	8	32	128	512	1024	4096
μ	0° .	61·8	82·7	128·2	180·0	229·1	256	335·5
	12·5° .	83·5	110·1	168·8	240·0	311·6	351·2	474
	25° .	106·0	138·6	210·0	301·5	400·5	489	636
	35° .	123·9	160·9	245·3	360·5	502·0	598	859
α	0° .	18·4	24·7	38·2	53·6	68·3	76·2	100·0
	25° .	16·6	21·7	33·0	47·4	62·8	76·8	100·0
	35° .	14·4	18·7	28·5	41·9	58·5	69·5	100·0

E. J. Schaefer and H. C. Jones made observations at higher temp., but the results are affected by the change from the violet to the green sulphate between 40° and 50°. H. H. Hosford and H. C. Jones gave for a modified green soln.:

v .	4	8	32	128	512	2048
μ	128·2	183·5	302·0	433·9	673·3	961·1
	160·0	227·8	354·4	522·7	811·1	1207·8
	189·6	262·9	417·4	606·0	977·3	1534·7

M. A. Graham gave for violet and the modified green soln.:

	v . .	16	32	64	128	256	512	1024
μ	violet 0°	85·37	100·0	117·7	139·2	166·6	194·2	232·2
	25°	151·5	177·1	211·8	255·0	310·2	379·5	476·9
μ	green 0°	168·1	187·7	211·2	233·2	255·2	270·8	282·1
	25°	245·7	285·2	336·5	390·4	450·7	515·0	568·5

W. R. Whitney observed that the modified green soln. has a higher conductivity than the violet, thus, $\frac{1}{30}N$-$Cr_2(SO_4)_3$ has a sp. conductivity 0·001489 in the violet state at 25° and 0·001927 in the modified green state. He also found that the conductivity with the addition of increasing proportions of sodium or barium hydroxide decreases to a minimum and thereafter increases. With a $\frac{1}{30}N$-soln., at 25°, the minimum is reached when the added sodium hydroxide is eq. to $\frac{1}{6}$th of the total sulphate present, or when the added barium hydroxide is eq. to one-third the total sulphuric acid. Hence, it is assumed that one-sixth of the sulphate in the green soln. is present as free sulphuric acid, and one-third as SO_4''-ions. This is in agreement with A. Recoura's assumption that the formation of the green soln. is attended by the formation of the salt $[Cr_4O(SO_4)_4]SO_4$. A. W. Thomas and M. E. Baldwin studied the $H^{\cdot}$-ion conc. of soln. of chromic sulphate. During the passage of an electric current through a soln. of the violet sulphate, chromium passes to the cathode; but in a soln. of the modified salt, the hydrogen ions migrate to the cathode much more quickly. T. W. Richards and F. Bonnet, and H. G. Denham found that no chromium goes to the anode in a modified green soln. so that no complex acid-ions are formed. The basic complex in the modified soln. seems to carry only one positive charge and has a transport number of 41 when that of SO_4'' is 70. F. C. Thompson and W. R. Atkin suggested that the active agent in tanning with chromic sulphate soln. is a negatively charged chromium complex, but F. L. S. Jones found that electrophoresis experiments on normal and basic soln. of chromic chloride and sulphate and of chrome-alum showed that anodic migration of chromium occurs only in basic sulphate soln., and therefore no such negative complex can exist in soln. of the chloride or of chrome alum. The subject was studied by H. B. Merrill and J. G. Niedercorn. P. Philipp found the magnetic susceptibility ranged from $31·93\times10^{-6}$ mass units for soln. of sp. gr. 1·3453 to $33·04\times10^{-6}$ mass units for soln. of sp. gr. 1·03086. T. Ishiwara, and K. Honda and T. Ishiwara gave for the anhydrous salt $13·3\times10^{-6}$ at 15·7°, and $9·7\times10^{-6}$ mass units at 300°; and for the enneahydrate, $4·5\times10^{-6}$ mass units at 16·9°, and $7·4\times10^{-6}$ at 434·8°.

According to F. P. Venable and F. W. Miller both the violet and the green, modified soln. are acid towards indicators owing to the hydrolysis. A. Recoura observed that distilling the aq. soln. furnishes an acidic distillate, while the dried salt does not lose acid at 100°. M. Krüger also found that alcohol poured over the green soln. takes up acid. F. P. Venable and F. W. Miller observed that eq. violet and green soln. required nearly the same amount of $\frac{1}{10}N$-NH_4OH to produce the first appearance of a permanent precipitate. Their conclusion was that the two soln. must therefore contain nearly the same proportion of acid, but as W. R. Whitney pointed out, the conclusion is wrong because alkali and ammonium hydroxides or carbonate turn the violet soln. green, and this change in colour precedes the formation of the permanent precipitate. C. R. C. Tichborne observed that if a soln. of chromic sulphate be heated to 177° under press. for 2 to 3 hrs., a precipitate of a basic sulphate is formed. G. Powarnin found that in dil. soln., chromium sulphate is more strongly hydrolyzed than aluminium sulphate; and that the hydrolysis is decreased in the presence of SO_4''-ions or Cl'-ions, and also by alcohol and formaldehyde. Many others have observed the hydrolysis of soln. of chromic sulphate. H. G. Denham measured the e.m.f., E, (H zero) of the cell $H_2 \mid Cr_2(SO_4)_{3\,\mathrm{violet}}, NH_4NO_3 \mid$ calomel electrode, and calculated the $H^{\cdot}$-ion conc., $[H^{\cdot}]$, and the percentage hydrolysis, x, as well as the ionization constant, K, where $K_1=[Cr(SO_4)(OH)][H^{\cdot}]/[Cr(SO_4)^{\cdot}]$, obtained from the hydrolytic reactions: $Cr_2(SO_4)_3+2H_2O \rightleftharpoons 2Cr(SO_4)OH+H_2SO_4$, or $Cr(SO_4)^{\cdot}+H_2O \rightleftharpoons Cr(SO_4)(OH)+H^{\cdot}$, for soln. of a mol of $Cr_2(SO_4)_3$ in v litres, at 25°,

v	6	8	16	32	64	128
E	−0·1417	−0·1444	−0·1533	−0·1604	−0·1713	−0·1653
$[H^{\cdot}]\times 10^2$	0·396	0·357	0·252	0·191	0·125	0·158
x	1·19	1·42	2·02	3·05	4·00	10·10
$K_1\times 10^4$	0·24	0·26	0·26	0·30	0·26	0·88

The great increase in the ionization constant with high dilution is taken to mean that another stage in the progressive hydrolysis occurs, namely, $Cr_2(SO_4)^{\cdot\cdot\cdot\cdot}+4H_2O \rightleftharpoons Cr_2(SO_4)(OH)_4+4H^{\cdot}$, for which he found that $K_2=[H^{\cdot}]^4[Cr_2(SO_4)(OH)_4]$-$[Cr_2(SO_4)^{\cdot\cdot\cdot\cdot}]$, or $K_2=0{\cdot}129\times 10^{-14}$. H. M. Vernon estimated the degree of ionization from the colour. M. A. Graham calculated from the conductivity of the violet soln. that the percentage hydrolysis is:

v	32	64	128	256	512	1024
x	1·78	3·19	4·76	8·08	16·24	33·98

At 0°, the violet soln. is only slightly hydrolyzed. The hydrolysis calculated from the effect on the velocity of inversion of cane sugar shows that the change from violet to green is much more rapid than the reverse process. A. Recoura found from the thermal data that in the modified green $\frac{1}{12}N$-soln., about one-sixth of the total sulphuric acid is free; and W. R. Whitney observed the effect of soln. of chromic sulphate on the hydrolysis of methyl acetate, and concluded that the green soln. possesses a hydrolyzing power equal to that of a mixture of one-sixth the eq. of free acid, with the corresponding amounts of the violet salt. The effects on the rate of inversion of cane sugar were too complex to enable a calculation to be made of the degree of hydrolysis of the soln. H. G. Denham calculated data for green modified soln. as in the case above cited for violet soln. and found

v	6	8	16	32	64	128
E	−0·0528	−0·0589	−0·0740	−0·0871	−0·0968	−0·1095
$[H^{\cdot}]$	0·1236	0·1005	0·05572	0·03342	0·02286	0·01393
x	37·1	40·2	44·6	53·4	72·9	88·8
K_1	0·18	0·21	0·23	—	—	—

The value of x is calculated on the assumption that the reaction is $[Cr_4(SO_4)_4](SO_4)_2+4H_2O \rightleftharpoons 2H_2SO_4+[Cr_4(SO_4)_4](OH)_4$; and K_1 is calculated for the formation of $[Cr_4(SO_4)_4](SO_4)(OH)_2$. As in the case of the violet soln., M. A. Graham calculated for the hydrolysis of the green modified soln., by the conductivity method,

v	16	32	64	128	256	512	1024
x	17·02	22·04	27·68	33·42	40·74	51·10	60·49

In both cases M. A. Graham's results are lower than those of H. G. Denham. The hydrolyses calculated from the effect on the inversion of cane sugar for soln. with $v=5$ and 10, are respectively 8·39 and 6·84 per cent., but the results are not so trustworthy. H. T. S. Britton calculated that a violet $0{\cdot}0050M$-soln. of chromic sulphate was hydrolyzed to the extent of 2·16 per cent., and a green $0{\cdot}0067M$-soln., 28·7 per cent. The electrometric titration curve is shown in Fig. 79. W. J. Chater and J. S. Mudd found a change in the p_H value at 2·3 and basicity 124. T. Svensson observed that a cell of chromic sulphate soln. gives an increased e.m.f. when illuminated. The change owing to the presence of neutral salt is dependent on the basicity. The difference in acidity caused by the neutral salt is a minimum at basicity 124. N. Demassieux and J. Heyrovsky obtained analogous polarization curves with chromic sulphates as were obtained with the chlorides (*q.v.*).

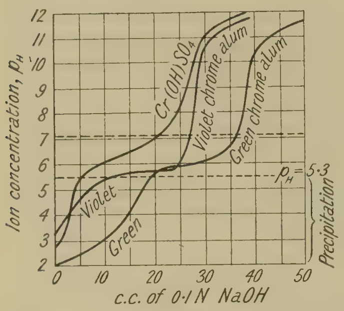


FIG. 79.—The Electrometric Titration Curves of Chromic Sulphate Solutions.

The penetration of gelatin jelly by chromium sulphate soln. is greater the greater the acidity. From his observations of the physical properties of the soln., and on those of T. W. Richards and F. Bonnet, H. G. Denham inferred that when the violet soln. is heated, the salt undergoes hydrolysis in the ordinary way; it is assumed that two mols. of the salt unite to form a complex: $2Cr_2(SO_4)_3 = [Cr_4(SO_4)_4](SO_4)_2$, and that the complex then hydrolyzes: $[Cr_4(SO_4)_4](SO_4)_2 + 2H_2O \rightleftharpoons [Cr_4(SO_4)_4]SO_4(OH)_2 + H_2SO_4$ with up to $\frac{1}{40}M$-soln., and on further dilution: $[Cr_4(SO_4)_4](SO_4)_2 + 4H_2O = 2H_2SO_4 + [Cr_4(SO_4)_4(OH)_4]$. D. M. Yost studied the rate of oxidation of soln. of chromic sulphate by potassium persulphate (*q.v.*). F. Hans found that chromic salts and silver salts (if soluble enough) react in accord with $Cr_2O_3 + 3Ag_2O = 2CrO_3 + 6Ag$. J. Poizat studied the action of chromic sulphate on the decomposition of hydrogen dioxide. W. R. Hodgkinson and C. C. Trench observed that chromium sulphate is reduced to a mixture of oxide and sulphide when heated in ammonia. F. Feigl found that a boiling soln. of chromic sulphate in alkali-lye is oxidized to chromate by charcoal (with oxygen in the pores); and G. Fuseya and co-workers discussed the formation of complex cations with chromic sulphate and glycine. W. Manchot and co-workers showed that soln. with 22·356 and 44·712 grms. $Cr_2(SO_4)_3$ per 100 c.c. dissolve respectively 31·8 and 18·2 c.c. of nitrous oxide per 100 c.c. of soln., and respectively 56·7 and 32·4 c.c. of acetylene.

L. N. Vauquelin, J. J. Berzelius, A. Schrötter, M. Siewert, H. Schiff, R. Bunsen, and C. R. C. Tichborne obtained precipitates of basic salts by the action of water on soln. of chromic hydroxide in sulphuric acid. In some cases the composition of the product approximated to $3Cr_2O_3.2SO_3$; H. Schiff obtained one approximating $3Cr_2O_3.4SO_3.12H_2O$; and M. Siewert, precipitates approximating to $5Cr_2O_3.8SO_3$, and to $5Cr_2O_3.12SO_3$. There is nothing to show that these products are anything more than arbitrary stages in the progressive hydrolysis of chromic sulphate. H. Schiff also obtained **chromic dioxysulphate,** $Cr_2O_2SO_4.nH_2O$, by dissolving a precipitated basic salt in dil. hydrochloric acid, and after diluting the soln., boiling it for some hours. A. Werner regarded it as **chromic dihydroxytetraquosulphate,** $[Cr(OH)_2(H_2O)_4]_2SO_4$, and obtained it by adding 10 grms. of pyridine to a soln. of 20 grms. of chrome-alum and 30 grms. of sodium sulphate in 300 grms. of water. The pale green, silky needles are but slightly soluble in water, and with organic and mineral acids form hexaquo-salts of the type $[Cr(H_2O)_6]X_3$. O. Grimm's observations on the chlorides are also applicable here.

A. Schrötter found that when dil. sulphuric acid sat. with hydrated chromic oxide is boiled for a long time and concentrated it furnishes a green soln. which is acidic to test-paper, and leaves on drying a green, amorphous mass from which the whole of the sulphate is expelled by ignition. H. Schiff added that at 100°, four mols. of water are given off and at a higher temp., one mol. A. Schrötter gave the formula of the compound dried at 50° to 60°, $2Cr(OH)SO_4.4H_2O$, but H. Schiff, in agreement with H. Löwel, gave $Cr_2(OH)_4SO_4.4H_2O$, **chromic tetrahydroxysulphate.** A. Schrötter found that a soln. of the salt appears ruby-red viewed by transmitted sunlight, or candle-light; and H. F. Talbot added that if the soln. which appears green by day-light, and red by candle-light be introduced into a prism with a refracting angle of 5° or 10°, and then placed between the eye and the candle-flame, red and blue images of the candle appear, and the rest of the visible spectrum is absorbed so that a kind of double refraction is produced. If the soln. be placed in a bottle and viewed by transmitted light, the two images overlap, the green predominates by daylight, and the red, by candle-light. A conc. soln. of the sulphate is rendered turbid by the addition of water, depositing the more basic 3 : 2-sulphate, and becoming paler in proportion to the amount of water added. On evaporation, however, the precipitate redissolves—when the dil. soln. filtered from the precipitate is heated, it deposits more of the 3 : 2-sulphate, which again disappears on boiling. A soln. of sp. gr. 1·219 and upwards deposits nothing when heated; a soln. of sp. gr. 1·166 becomes turbid at 57°; a soln. of sp. gr. 1·037—1·031, at 64°; one of sp. gr. 1·002, at 45°; and one of sp. gr. 1·001, at 55°; while still more dil. soln. remain clear when boiled. According to H. Löwel, if the green soln. be treated with as much acid as it already contains, ammonia then produces a dark green precipitate which is only slightly soluble in ammonia. M. Siewert found that when soln. of the violet salt is boiled with an excess of hydrated chromic oxide, and the green soln. evaporated almost to the point of solidification, it becomes turbid when water is added, but clarifies again on evaporation. Absolute alcohol precipitates from the soln. a green syrup of the 1 : 2-sulphate, and it forms a clear soln. with water. The soln. does not become turbid when boiled, but gives the 1 : 2-sulphate as a precipitate when alcohol is added. B. Cabrera and S. P. de Rubies studied the magnetic qualities of green and violet **chromic oxydisulphate,** $Cr_2O(SO_4)_2.nH_2O$, and found that they change when the soln. is kept for some time. It is suggested that this is due to the changes: $[Cr_2(SO_4)_2O] \rightarrow [Cr_2(SO_4)O]SO_4 \rightarrow [Cr_2O](SO_4)_2$. According to L. and P. Wöhler and W. Plüddemann, the oxydisulphate, obtained by heating the basic sulphate to 280° in a current of carbon dioxide, has a dissociation press. of 91 mm. at 340°, and 191 mm. at 372°; and the heat of dissociation is 21·97 Cals. Likewise, **chromic trioxytrisulphate,** $Cr_4O_3(SO_4)_3$, obtained by heating the basic sulphate to 450° or 460° in a current of carbon dioxide, has a dissociation press. of 146 mm. at 640°, and 400 mm. at 660°; the heat of dissociation is 61·62 Cals.

According to A. Colson, **chromic oxypentasulphate,** $Cr_4O(SO_4)_5.nH_2O$, with *two masked* SO_4*-radicles* is obtained by treating a cold soln. of 100 grms. of chrome-alum in 4 litres of water of ammonia; digesting an excess of the washed precipitate in sulphuric acid; and evaporating the soln. in vacuo. Only three of the five sulphate radicles are precipitated from a soln. of the salt by barium chloride. The salt in alcoholic soln. has the same composition as the solid. If the soln. of this salt is slowly crystallized, by evaporation in dry air, it yields the oxypentasulphate, $Cr_4O(SO_4)_5.12H_2O$, with *three masked* SO_4*-radicles.* A. Colson said that when a soln. of the violet sulphate is heated, it forms the oxypentasulphate, $HSO_4(CrSO_4)_2.O.(CrSO_4)_2.O.CrSO_4$, in which there are *four masked* SO_4*-radicles.* If the soln. is boiled and suddenly cooled, it yields the sulphate with all its sulphate radicles masked.

According to P. Nicolardot, when a violet soln. is boiled, and the resulting green liquor is heated with barium sulphate, part of the sulphuric acid is precipitated, and when the filtrate is allowed to evaporate spontaneously, there remains chromic oxypentasulphate, $Cr_2O_3.2{\cdot}5SO_3.7{\cdot}5H_2O$, that is, $Cr_4O(SO_4)_5.15H_2O$, with *all five* SO_4*-radicles masked.* This salt appears as a non-crystalline solid, readily soluble in water to form a green soln., but insoluble in alcohol or acetone, and precipitated from aq. soln. by these liquids. Soln. of the salt do not yield precipitates with barium chloride or with sodium phosphate; it differs in this respect from the sulphate of sulphochromyl hydroxide described, but not isolated, by A. Recoura. According to A. Colson, the equilibrium indicated in the following equation, $2Cr_2(SO_4)_3+H_2O \rightleftharpoons H_2SO_4+Cr_4O(SO_4)_5$, is only relatively stable, and the pentasulphate, $Cr_4O(SO_4)_5$, is acted on by boiling water with momentary production of a fresh quantity of acid, thus: $Cr_4O(SO_4)_5+H_2O \rightleftharpoons Cr_4O_2(SO_4)_4+H_2SO_4$. This is proved by the repeated boiling of a 0·1N-soln. of the normal green sulphate, $Cr_2(SO_4)_3.10H_2O$, cooling very rapidly, and then adding baryta-soln. The amount of heat developed in the reaction shows that each successive boiling after the first liberates sulphuric acid according to the second equation.

C. F. Cross and A. F. Higgin obtained an acid salt approximating $4Cr_2O_3.6SO_3.7H_2SO_4$, by heating chromic oxide with conc. sulphuric acid. The grey powder is insoluble in water, and is attacked with difficulty by alkali-lye. According to M. Traube, and A. Schrötter, a pale puce or grey powder is formed when a green mush of conc. sulphuric acid and a basic chromic sulphate or hydrated oxide is heated until sulphuric acid begins to volatilize: if a large proportion of sulphuric acid is employed, a green soln. is obtained, which when heated becomes colourless, and deposits the puce or grey powder. The product is washed with water and dried. A. Schrötter regarded it as the normal sulphate, but M. Traube, and M. Siewert showed that it is rather **chromic dihydroheptasulphate,** $2Cr_2(SO_4)_3.H_2SO_4$. A. Étard supposed the compound to be constituted $Cr_2(SO_4)_6Cr_2.H_2SO_4$, or $HSO_4.Cr_2(SO_4)_5Cr_2.HSO_4$; and G. N. Wyrouboff, $[Cr_2O_3(SO_2)_4O_4Cr_2O_3(SO_2)_3O_2(OH)_2]_3$. M. Traube also obtained the same salt contaminated with some potassium salt by the action of conc. sulphuric acid on potassium dichromate and chrome-alum; and T. Klobb, by the action of the acid on the ammonium chromic sulphate. M. Traube said that the powder is sometimes so fine that it will pass through filter-paper; and will remain suspended in water a considerable time, but can be rapidly precipitated by the addition of various salts—*e.g.* ammonium carbonate, potassium sulphate, etc. The powder appears grey by daylight, and green by candle-light; and A. Schrötter said that the powder may appear a very light red by diffused daylight; pale green by sunlight; and verdigris-green by candle-light. Every time it is heated, it appears puce-coloured. When heated to redness, it gives off all its sulphuric acid; and, according to M. Traube, a pyrophoric mixture of chromic sulphide and oxide may be formed. When heated in hydrogen it yields water, hydrogen sulphide, sulphur, and chromic oxide; while a current of hydrogen sulphide converts the heated salt into black chromic sulphide, with the formation of water, sulphur, and sulphur dioxide. It is insoluble in cold water, but when boiled for a long time with water, or when allowed to stand for a long time in contact with water, some of it passes into soln. It is insoluble in aq. ammonia and in strong mineral acids—*e.g.* hydrochloric, sulphuric, and nitric acids, or in aqua regia. The salt is readily decomposed by fused alkali hydroxide, or by a boiling soln. of the hydroxide or carbonate.

R. F. Weinland and R. Krebs prepared **chromic dihydrotetrasulphate,** $Cr_2(SO_4)_3.H_2SO_4.nH_2O$, by the action of an excess of conc. sulphuric acid on a soln. of chrome-alum. The *hexadecahydrate* separates in the *violet form* if the mixture is made with well-cooled liquids; columnar crystals separate from a soln. of 100 mols of sulphuric acid and one of chrome-alum when evaporated in vacuo, while if the mixture is made with warm soln., the *green form* is produced in acicular crystals. Only with the violet soln. is all the sulphuric acid precipitated by barium chloride. The salt loses no water if the salt be kept over sulphuric acid in vacuo. A soln. of a mol of the violet sulphate in 124·7 litres of water has a conductivity of 116, and this value does not change with time; on the other hand, a soln. of the green salt of nearly the same conc. has a conductivity of 76·5 which in 2 hrs. rises to 80·8, in 5 hrs. to 93·2, and in 24 hrs. to 101·8. It is therefore inferred that the violet salt is to be formulated $[Cr_2(H_2O)_{16}](SO_4)_3(H_2SO_4)$, and that with the green salt, some sulphate is contained within the co-ordinated group. If the original components interact at —15°, long, tabular, violet crystals of the *tetracosihydrate* are formed, $[Cr_2(H_2O)_{16}](SO_4)_3(H_2SO_4).8H_2O$, or $[Cr(H_2O)_8](SO_4(HSO_4).4H_2O$. This salt can be regarded as being related to chrome-alum since both contain the same number of water mols., and in both the sulphate-radicle is all precipitated by barium sulphate: $HCr(SO_4)_2.12H_2O$, and $KCr(SO_4)_2.12H_2O$. Chrome-alum loses 6 mols. of water over sulphuric acid in vacuo, while hydrochromodisulphuric acid loses 4 mols., yielding the hexadecahydrate. Still further, if 140 mols of sulphuric acid be employed to one mol of sulphate, **chromic tetrahydropentasulphate,** $Cr_2(SO_4)_3.2H_2SO_4.18H_2O$, or $[Cr_2(H_2O)_{18}](SO_4)_3(H_2SO_4)_2$, is formed in rectangular plates. This *violet form* of the salt becomes greyish-green when heated to 100°, with the loss of some water. Barium chloride does not precipitate all the sulphate from the green aq. soln., but it does so from the violet soln. Consequently, some sulphate radicle is contained within the co-ordination group of the green salt.

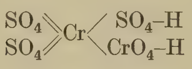
According to A. Recoura, green chromic sulphate can unite with one, two, and three mols. of sulphuric acid, or metal sulphates to form complex **chromisulphuric acids,** or their salts. The acids are prepared by evaporating to dryness on a water-bath a soln. of a mol of green chromic sulphate with one, two, or three mols of sulphuric acid, and heating the green product for a long time to 110° to 120°. No sulphate is precipitated when barium chloride is first added to aq. soln. of the acids. There are thus obtained **chromitetrasulphuric acid,** $Cr_2(SO_4)_3.H_2SO_4.nH_2O$, or $H_2[Cr_2(SO_4)_4]nH_2O$, or, according to W. R. Whitney, $[Cr_2(H_2O)_4(SO_4)]H_2$; **chromipentasulphuric acid,** $Cr_2(SO_4)_3.2H_2SO_4.nH_2O$, or $H_4[Cr_2(SO_4)_5].nH_2O$, or, according to W. R. Whitney, $[Cr_2(H_2O)_2(SO_4)_5]H_4$; and **chromihexasulphuric acid,** $Cr_2(SO_4)_3.3H_2SO_4.nH_2O$, or $H_6[Cr(SO_4)_6].nH_2O$, or, according to W. R. Whitney, $[Cr(SO_4)_6]H_6$. G. N. Wyrouboff regarded these acids as esters of the green sulphate in which two hydroxyl radicles are replaced by chromosulphuric acid. These acids are accordingly represented respectively by $[Cr_2O(OH)_4(SO_2)_4]O(OH)_6$; by $[Cr_2O(OH)_4(SO_2)_5]O_2(OH)_6$; and by $[Cr_2O(OH)_4(SO_2)_6]O_3(OH)_6$. According to A. Recoura, the proportion of contained water is dependent on the duration of the heating at 110° to 120°, and they lose no sulphuric acid below 170°. E. Moles and M. Crespi gave for the sp. gr. of the acid $HCr(SO_4)_2$, 2·724 at 25°/4°, and 90·5 for the mol. vol.; for the acid $HCr(SO_4.H_2O)_2$, they found the sp. gr. 2·516, and the mol. vol. 111·5; and for $H[Cr(H_2O)_6](SO_4.H_2O)_2$, respectively 2·009 and 195. They also observed that the acid $H[Cr(H_2O)_6](SO_4.H_2O)_2$ loses 6·03 mols. of water at 120°, and $HCr(SO_4.H_2O)_2$, 1·91 mols. at 350°. According to A. Recoura, the acids are stable when dry, and they are freely soluble in water forming green soln. The basicity of the acids just indicated accords with the thermal values of the neutralization of soln. of the respective acids with 2, 4, and 6 mols. of a soln. of sodium hydroxide—one mol per 20 litres: $(H_2[Cr_2(SO_4)_4],2NaOH)=33{\cdot}3$ Cals.; $(H_4[Cr(SO_4)_5],4NaOH)=2\times33$ Cals.; and $(H_6[Cr(SO_4)_6],6NaOH)=3\times32$ Cals. When $(H_2SO_4,2NaOH)=30{\cdot}8$ Cals. under similar conditions. The formulæ are also in accord with the fact that freshly prepared soln. do not show the reactions of chromium or sulphates with mild reagents like sodium phosphate and barium chloride. In course of time, particularly when heated, or when treated with stronger reagents like sodium hydroxide, the soln. do give the reactions of chromium and of sulphuric acid. W. R. Whitney found the electrical conductivity, λ mhos, of soln. a gram-equivalent in *v* litres at 0° to be close to the values for sulphuric acid of the same conc.,

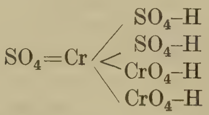
v	. . . . .	202	404	808	1616	3232
λ	$\frac{1}{2}H_2SO_4$	210·7	223·7	236·0	245·5	249·2
	$\frac{1}{2}H_2[Cr_2(SO_4)_3(H_2SO_4)]$	210·6	223·1	232·5	241·0	250·9
	$\frac{1}{4}H_4[Cr_2(SO_4)_3(H_2SO_4)_2]$	210·9	222·9	231·5	240·6	260·5
	$\frac{1}{6}H_6[Cr_2(SO_4)_3(H_2SO_4)_3]$	210·7	222·3	236·0	244·0	250·8

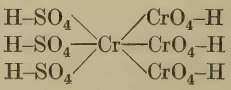
Consequently, W. R. Whitney inferred that the ionization, the velocities of transport of the anions, and the strengths of the four acids are approximately the same; similar conclusions were drawn from the action of the four acids on the hydrolysis of methyl acetate. Determinations of the f.p. show that the number of molecules in soln. of these acids is conditioned by the free sulphuric acid present in the soln. The f.p. of sulphuric acid is the same as that of one of these acids with the same content of free sulphuric acid—*i.e.* acid not bound to the chromium. Hence, chromic sulphate does not act as individual compound, but it forms complexes in agreement with the results deduced from the chemical behaviour of the complexes. When the soln. are kept for some time, the f.p. data show that there is an increase in the number of molecules. For an isomeric form of chromic tetrasulphuric acid, *vide infra.*

A. Recoura attempted to prepare chromisulphuric acids with more than three mols of sulphuric acid per mol. of chromic sulphate, but found that the products have quite a different character. Thus, when a soln. of a mol of the green sulphate with 4, 5, or 6 mols. of sulphuric acid is evaporated on a water-bath, and the resulting dark green syrup is heated for some days at 115°, **chromipolysulphuric acids**—respectively **chromiheptasulphuric acid,** $Cr_2(SO_4)_3.4H_2SO_4$; **chromioctosulphuric acid,** $Cr_2(SO_4)_3.5H_2SO_4$; and **chromienneasulphuric acid,** $Cr_2(SO_4)_3.6H_2SO_4$—are obtained in the form of transparent, green glasses which form yellowish-green soln. with water. These soln. form transparent, gelatinous masses after standing a few days; they are coagulated at 100°; on the addition of strong acids they furnish green flecks; and they give green, insoluble, flocculent precipitates when treated with soln. of the salts of the metals. In this reaction the complex is reduced to a chromitetrasulphate, $MSO_4.Cr_2(SO_4)_3$ or $Cr(SO_3)_4O_2(OH)_2$ and the excess sulphate is set free as sulphuric acid; thus, chromiheptasulphuric acid reacts with cupric chloride: $[Cr_2(SO_4)_3(H_2SO_4)_4]+CuCl_2=3H_2SO_4+2HCl+[Cr_2(SO_4)_4]Cu$. A. Recoura also prepared the chromitetrasulphuric acid by heating chromiheptasulphuric acid to 140°–150° until it no longer loses weight, and has lost 3 mols. of sulphuric acid. The grey powder is an isomeric form of the chromitetrasulphuric acid indicated above. It forms a greenish-yellow, opalescent or colloidal soln. with water, and with soln. of the metal salts, insoluble chromitetrasulphates. Chromitetrasulphuric acid, $Cr_2O_2(SO_3)_4(OH)_2$, or $[Cr_2(SO_4)_4]H_2$, is dibasic, and it is a stronger acid than sulphuric acid. Strong acids precipitate it as a gelatinous mass from soln. of its salts. The acid can be transformed into its isomeric form by boiling with water; and with boiling alkali-lye, chromites are formed. G. N. Wyrouboff believed that these chromipolysulphuric acids are not chemical individuals, but mixtures of sulphuric acid with the chromitetrasulphuric acid.

A. Recoura showed that the green chromic sulphate can unite with one, two, or three mols. of chromic acid to form **chromitrisulphatochromic acids.** These are analogous to the chromisulphuric acids. Thus, there is **chromitrisulphatochromic acid,** $Cr_2(SO_4)_3.H_2CrO_4$, or $H_2[Cr_2(SO_4)_3(CrO_4)]$; **chromitrisulphatodichromic acid,** $Cr_2(SO_4)_3.2H_2CrO_4$, or $H_4[Cr_2(SO_4)_3(CrO_4)_2]$; and **chromitrisulphatotrichromic acid,** $Cr_2(SO_4)_3.3H_2CrO_4$, or $H_6[Cr_2(SO_4)_3(CrO_4)_3]$. The constitutions may also be represented respectively by the formulæ:







These acids form dark brown amorphous masses which, in freshly prepared, dil. soln. exhibit the characteristic reactions of neither SO_4''—nor CrO_4''—radicles, slowly decompose when they do show the reactions of these radicles. Arguing by analogy, and from some observations on the heats of neutralization, it is inferred that the constitution of the chromisulphatochromic acids resembles that of the chromisulphuric acids. If the alkali chromates are employed in place of chromic acid in the preparation of these products then the corresponding chromisulphatochromates are formed. J. Poizat studied the action of chromimono-, -di-, and tri-sulphuric acids on hydrogen dioxide.

According to G. N. Wyrouboff, when an aq. soln. of chromisulphuric acid is heated, a coagulum is formed which he called *chromium sulphochromate*, $[Cr_2O_2(OH)_4(SO_2)_4O_2(OH)_2]Cr_2(OH)_6$, and which is identical with that obtained by precipitating a violet salt of chromium in the cold with sulphochromic acid. If this is maintained for some time in contact with boiling water, it becomes hydrated, dissolves slowly, and finally passes entirely into a soln. of the green sulphate. Chromium sulphochromate, when heated at 120°, becomes soluble in water and the soln. yields insoluble precipitates with metallic salts, *chromosulphochromates* being formed. When chromium sulphochromate is treated with hydrochloric acid, what he called *chromosulphochromic acid*, $[Cr_2O_2(OH)_4(SO_2)_4O_3.Cr_2O(OH)_2(SO_2)_3(OH_6][(OH)_2$, is precipitated as a dark green, gelatinous mass which dissolves in water, yielding an opalescent soln. On adding 2 mols of sulphuric acid and a little water to 1 mol of chromium sulphochromate, evaporating on the water-bath, and heating for some hours at 120°, *chromodisulphochromic acid*, $[Cr_2O_2(OH)_4(SO_2)_4O_3]_2Cr_2O(OH)_2(SO_2)_3(OH)_4(OH)_4.H_2O$, is obtained, which yields an insoluble salt with iron. With sulphochromic acid, chromium sulphochromate yields a chromosulphodichromate. If chromium sulphate is heated with an excess of sulphuric acid to a temp. not exceeding 150°, a clear green, gelatinous precipitate of sulphochromic acid is formed; on continuing the heating and at the same time allowing the temp. to rise, the green precipitate gradually changes into a heavy, greyish-yellow powder, soluble in water, yielding a milky, strongly acid soln. The same substance is obtained by heating sulphochromic acid for some time at 250°, and is the first anhydride of a polymeride of chromosulphochromic acid. Although sulphochromic acid forms insoluble compounds with the metals, it does not give precipitates with all the salts of the metals. Thus, it gives a precipitate with a soln. of mercuric nitrate or acetate, but not with mercuric bromide. This is explained by saying that the last-named salt is an anhydride and not a normal salt.

The products obtained by J. L. Gay Lussac[3] by the action of sulphuric acid on chromic anhydride, were shown by J. Fritzsche, and P. Plantamour to be mechanical mixtures. J. Meyer and V. Stateczny found the f.p. of mixtures of chromic acid and water-free H_2SO_4 to be:

CrO_3 .	0	0·16	1·2	2·02	3·13	4·17	5·37	8·66 per cent.
F.p. .	10·45°	10·2°	8·6°	5·8°	7·6°	8·8°	9·6°	9·8°

The eutectic at 5·5° corresponds with 2·2 per cent. CrO_3. A. W. Rakowsky and D. N. Tarassenkoff found that the compound decomposes at ordinary temp. with a marked change of colour when the humidity exceeds 1·7 per cent. W. Ipatieff and A. Kisseleff obtained **potassium trisulphatodichromate,** $2KCrO_4.Cr_2(SO_4)_3.H_2O$, by the action of hydrogen under press. on a soln. of potassium dichromate (*q.v.*). P. A. Bolley added chromium trioxide to conc. sulphuric acid, until no more dissolved, the resulting dark brown oil forms a pale brown, granular mass in a few days. A. Schrötter obtained a yellowish-brown substance to which he gave the formula $CrO_3.3SO_3$; and A. Pictet and G. Karl heated a mixture of sulphur and chromium trioxides in a sealed tube and obtained a yellowish-brown mass of $CrO_3.SO_3$, sometimes regarded as **chromyl sulphate,** $CrO_2(SO_4)$. The products are unstable in air, and liberate chromium trioxide by the action of moisture. The observations of L. F. Gilbert and co-workers, and A. W. Rakowsky and D. N. Tarassenkoff on the solubility of chromium trioxide in soln. of sulphur trioxide at 25° and 45° were discussed in connection with chromium trioxide. The results of L. F. Gilbert and co-workers are shown graphically in Fig. 80, for the ternary system: CrO_3–SO_3–H_2O at 25°. There are three solid phases CrO_3; $CrO_3.SO_3$; and what is thought to be the *monohydrate*, $CrO_3.SO_3.H_2O$. Chromyl sulphate is usually brown and minutely crystalline, and sometimes amorphous; the hydrate is also amorphous. Both compounds are very hygroscopic, and liberate scarlet chromium trioxide on exposure to air.

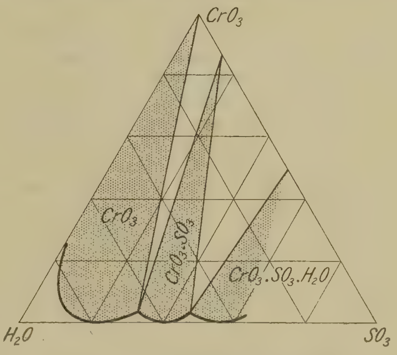


FIG. 80.—The Ternary System: CrO_3–SO_3–H_2O at 25°.

J. Meyer and V. Stateczny said that the orange precipitate which gradually forms from soln. of chromium trioxide in 95 to 100 per cent. H_2SO_4 is **chromatosulphuric acid,** H_2CrSO_7, or $H_2[CrO_3(SO_4)]$, and that it appears as a dark orange powder which reacts very energetically with water to form a brick-red soln. of chromic and sulphuric acids. The acid can be preserved over phosphorus pentoxide, or in a sealed tube. It is decomposed in light. It is insoluble in carbon disulphide and similar liquids; it is gradually reduced by ether, ligroin, and benzene. It darkens in colour when heated, it sinters at 168°–170°, and at 190° forms a blood-red liquid and then decomposes with the evolution of oxygen. It is a powerful oxidizing agent—a drop of alcohol is inflamed by the acid; and it forms chromic oxide with the evolution of sulphur dioxide when treated with aldehyde. Naphthalene, and phenol are carbonized; anthracene yields acetic acid; and a mixture of sugar and potassium chlorate is exploded by the acid. It does not form salts by direct neutralization. H. Schiff prepared **potassium chromatosulphate,** K_2CrSO_7, or $K_2[CrO_3(SO_4)]$, by melting potassium sulphate or hydrosulphate with potassium chlorochromate; and J. Meyer and V. Stateczny, by the reaction $K_2Cr_2O_7+2KHSO_4=H_2O+2K_2CrSO_7$. They also prepared **ammonium chromatosulphate,** $(NH_4)_2[CrO_3(SO_4)]$, and **sodium chromatosulphate,** $Na_2[CrO_3(SO_4)]$, in a similar manner. By heating a mixture of barium chromate and sulphur trioxide in a sealed tube for 3 hrs. at 120°, **barium chromatosulphate,** $Ba[CrO_3(SO_4)]$, was obtained; and **strontium chromatosulphate,** $Sr[CrO_3(SO_4)]$, by heating to 160° for 3 hrs. a mixture of strontium sulphate and chromium trioxide; and similarly with **calcium chromatosulphate,** $Ca[CrO_3(SO_4)]$. B. Cabrera and S. P. de Rubies studied the magnetic properties of the products formed by the addition of sulphuric acid to the oxychromic salts.

References.

[1] E. M. Péligot, *Ann. Chim. Phys.*, (3), **12**. 546, 1844; M. Berthelot, *ib.*, (4), **9**. 385, 1866; H. Moissan, *ib.*, (5), **25**. 410, 1882; *Bull. Soc. Chim.*, (2), **37**. 296, 1882; *Compt. Rend.*, **92**. 793, 1881; C. Laurent, *ib.*, **131**. 111, 1900; *De l'action du sulfate chromeux sur les sulfates métalliques*, Rennes, 1901; A. Burger, *Ber.*, **39**. 4070, 1906; W. Traube and W. Passarge, *ib.*, **46**. 1505, 1913; J. M. van Bemmelen, *Rec. Trav. Chim. Pays-Bas*, **6**. 202, 1887; B. Cabrera and S. P. de Rubies, *Anal. Fis. Quim.*, **17**. 149, 1919; A. Asmanoff, *Zeit. anorg. Chem.*, **160**. 209, 1927; F. Allison and E. J. Murphy, *Journ. Amer. Chem. Soc.*, **52**. 3796, 1930.

[2] L. N. Vauquelin, *Journ. Phys.*, **45**. 393, 1794; **46**. 152, 311, 1798; *Journ. Mines*, **6**. 737, 1797; *Nicholson's Journ.*, **2**. 387, 441, 1799; *Phil. Mag.*, **1**. 279, 361, 1798; **2**. 74, 1798; *Ann. Chim. Phys.*, (1), **25**. 21, 194, 1798; (1), **70**. 70, 1809; E. Kunheim, *Ueber die Einwirkung des Lichtbogens auf Gemische von Sulfaten mit Kohle*, Berlin, 39, 1900; J. J. Berzelius, *Pogg. Ann.*, **1**. 34, 1824; *Schweigger's Journ.*, **22**. 53, 1818; F. Brandenburg, *ib.*, **13**. 274, 1815; P. A. Bolley, *Journ. Pharm. Chim.*, (3), **9**. 226, 1846; *Liebig's Ann.*, **56**. 113, 1845; H. Schiff, *ib.*, **124**. 167, 1862; M. Siewert, *ib.*, **126**. 97, 1863; M. Traube, *ib.*, **66**. 168, 1848; A. Schumann, *ib.*, **187**. 305, 1877; R. Robl, *Zeit. angew. Chem.*, **39**. 608, 1926; E. N. Gapon, *Journ. Chim. Phys.*, **25**. 154, 1925; O. Hagen, *Pogg. Ann.*, **106**. 33, 1859; *Ann. Chim. Phys.*, (3), **56**. 367, 1859; J. Fritzsche, *Bull. Acad. St. Petersburg*, (1), **6**. 181, 1840; *Journ. prakt. Chem.*, (1), **19**. 176, 1840; *Pogg. Ann.*, **50**. 540, 1840; J. L. Gay Lussac, *Ann. Chim. Phys.*, (2), **16**. 102, 1821; A. Colson, *ib.*, (8), **12**. 458, 1907; *Compt. Rend.*, **140**. 42, 372, 1451, 1905; **141**. 119, 1024, 1905; **142**. 402, 1906; **144**. 179, 206, 325, 637, 1907; **145**. 250, 1907; *Bull. Soc. Chim.*, (4), **1**. 438, 889, 1907; (4), **3**. 90, 1908; (4), **9**. 862, 1911; (4), **33**. 67, 1923; A. Recoura, *ib.*, (3), **7**. 200, 1892; (3), **9**. 586, 1893; (3), **15**. 315, 1896; *Ann. Chim. Phys.*, (7), **4**. 505, 1895; *Compt. Rend.*, **84**. 1090, 1877; **112**. 1439, 1891; **113**. 857, 1891; **117**. 31, 101, 1893; **118**. 1146, 1894; **169**. 1163, 1919; **170**. 1494, 1920; **174**. 1460, 1922; **183**. 719, 1926; E. Feytis, *ib.*, **156**. 886, 1913; G. Massol and A. Faucon, *ib.*, **157**. 332, 1913; A. Schrötter, *Pogg. Ann.*, **53**. 516, 1841; R. Bunsen, *ib.*, **155**. 230, 1875; P. Plantamour, *Berzelius' Jahresb.*, **20**. ii, 101, 1840; H. Löwel, *Journ. Pharm. Chim.*, (3), **4**. 321, 401, 1845; P. Nicolardot, *Compt. Rend.*, **145**. 1338, 1907; V. N. Ipatieff and B. A. Mouromtseff, *ib.*, **183**. 505, 1926; A. Mailfert, *ib.*, **94**. 797, 860, 1186, 1882; H. Baubigny, *ib.*, **98**. 146, 1884; A. Étard, *ib.*, **80**. 1306, 1875; **84**. 1090, 1877; **86**. 1399, 1878; **87**. 602, 1878; **120**. 1057, 1895; *Bull. Soc. Chim.*, (2), **31**. 200, 1879; J. Poizat, *ib.*, (4), **33**. 1606, 1923; T. Klobb, *ib.*, (3), **9**. 667, 1893; E. Kopp, *Compt. Rend.*, **18**. 1156, 1844; F. M. Strong, *ib.*, **150**. 1172, 1910; P. A. Favre and C. A. Valson, *ib.*, **77**. 579, 803, 1873; A. Sénéchal, *ib.*, **156**. 552, 1913; **159**. 243, 1914; *L'étude physico-chimique des sels chromiques*, Paris, 1913; G. Urbain and A. Sénéchal, *Introduction à la chimie des complexes*, Paris, 361, 1913; G. T. Gerlach, *Zeit. anal. Chem.*, **28**. 490, 1889; A. Pictet and G. Karl, *Bull. Soc. Chim.*, (4), **3**. 114, 1908; *Arch. Sciences Genève*, (4), **26**. 437, 1908; A. W. F. Sprung, *ib.*, (2), **53**. 120, 1875; J. L. Soret, *ib.*, (3), **13**. 5, 1885; (3), **20**. 517, 1888; (4), **3**. 376, 1897; *Compt. Rend.*, **99**. 867, 1884; **101**. 156, 1885; A. Kling, D. Florentin and E. Hachet, *ib.*, **159**. 60, 1914; G. Magnanini, *Gazz. Chim. Ital.*, **25**. ii, 378, 1895; A. Rosenstiehl, *Bull. Soc. Chim.*, (3), **15**. 956, 1896; (4), **1**. 774, 1907;

G. N. Wyrouboff, *Ann. Chim. Phys.*, (8), **13**. 523, 1908 ; *Bull. Soc. Chim.*, (3), **27**. 676, 1902 ; A. Hébert, *ib.*, (4), **1**. 1026, 1907 ; L. F. Nilson and O. Petterson, *Oefvers. Akad. Stockholm*, **37**. 6, 1880 ; *Proc. Roy. Soc.*, **31**. 46, 1881 ; *Chem. News*, **43**. 17, 1881 ; *Compt. Rend.*, **91**. 232, 1880 ; *Ber.*, **13**. 1462, 1880 ; A. Werner, *ib.*, **41**. 3447, 1908 ; A. Werner and A. Gubser, *ib.*, **34**. 1592, 1901 ; A. Gubser, *Ueber die Hydrate des Chromchloride*, Zürich, 1900 ; A. Violi, *Ber.*, **10**. 293, 1877 ; L. and P. Wöhler and W. Plüddemann, *ib.*, **41**. 703, 1908 ; W. Plüddemann, *Eine neue Methode zur Tensionsbestimmung von Sulfaten*, Berlin, 1907 ; C. F. Cross and A. F. Higgin, *Journ. Chem. Soc.*, **41**. 113, 1882 ; L. F. Gilbert, H. Buckley and I. Masson, *ib.*, **121**. 1934, 1922 ; F. Fichter and E. Brunner, *ib.*, 1862, 1928 ; M. D. Dougal, *ib.*, **69**. 1527, 1896 ; H. T. S. Britton, *ib.*, **127**. 2120, 1925 ; *Ind. Chemist*, **3**. 452, 1927 ; R. Krebs, *Ueber Chromchloridsulfate und Chromsulfate*, Tübingen, 1906 ; Y. Shibata, *Journ. Coll. Science, Japan*, **41**. 6, 1919 ; R. F. Weinland and R. Krebs, *Zeit. anorg. Chem.*, **49**. 157, 1906 ; H. G. Denham, *ib.*, **57**. 361, 1908 ; W. W. Rakowsky and D. N. Tarassenkoff, *ib.*, **174**. 91, 1928 ; J. H. Gladstone, *Phil. Mag.*, (5), **20**. 162, 1885 ; H. F. Talbot, *ib.*, (3), **4**. 112, 1834 ; G. O. Higley, *Journ. Amer. Chem. Soc.*, **26**. 626, 1904 ; F. P. Venable and F. W. Miller, *ib.*, **20**. 484, 1898 ; D. M. Yost, *ib.*, **48**. 152, 1926 ; A. W. Thomas and M. E. Baldwin, *ib.*, **41**. 1981, 1919 ; W. R. Whitney, *ib.*, **21**. 1075, 1899 ; *Zeit. phys. Chem.*, **20**. 40, 1896 ; G. D. van Cleeff, *Journ. prakt. Chem.*, (2), **23**. **58**. 69, 1881 ; G. Powarnin, *Journ. Russ. Phys. Chem. Soc.*, **41**. 1014, 1909 ; C. R. C. Tichborne, *Proc. Irish Acad.*, **1**. 169, 1874 ; *Chem. News*, **24**. 199, 209, 1871 ; H. M. Vernon, *ib.*, **66**. 104, 114, 141, 152, 1892 ; L. G. Winston and H. C. Jones, *Amer. Chem. Journ.*, **46**. 368, 1911 ; E. J. Schaeffer and H. C. Jones, *ib.*, **49**. 207, 1913 ; H. H. Hosford and H. C. Jones, *ib.*, **46**. 240, 1911 ; W. Schindler and K. Klanfer, *Collegium*, 97, 1928 ; G. Grasser, *ib.*, 356, 1921 ; H. B. Merrill, J. G. Niedercorn and R. Quarck, *Journ. Amer. Leather Chem. Assoc.*, **23**. 187, 1928 ; F. C. Thompson and W. R. Atkin, *Journ. Soc. Leather Trades Chem.*, **6**. 207, 1922 ; W. J. Chater and J. S. Mudd, *ib.*, **12**. 272, 1928 ; F. L. S. Jones, *Journ. Ind. Eng. Chem.*, **15**. 265, 1923 ; H. B. Merrill and J. G. Niedercorn, *ib.*, **21**. 252, 1929 ; O. Nydegger, *Brit. Pat. No.* 198645, 1923 ; A. W. Gregory, *ib.*, 17672, 1912 ; K. Schorlemmer, *Collegium*, 345, 371, 1917 ; 145, 1918 ; 5, 1919 ; *Journ. Soc. Leather Trades Chem.*, **2**. 57, 1918 ; T. Svensson, *Arkiv. Kemi Min. Geol.*, **7**. 19, 1919 ; *Lichtelektrische Untersuchungen an Salzlösungen*, Stockholm, 1919 ; K. H. Butler and D. McIntosh, *Trans. Roy. Soc. Canada*, (3), **21**. 19, 1927 ; L. R. Ingersoll, *Journ. Amer. Opt. Soc.*, **6**. 663, 1922 ; H. C. Jones and W. W. Strong, *Phys. Zeit.*, **10**. 499, 1909 ; *A Study of the Absorption Spectra*, Washington, 1910 ; H. C. Jones and E. Mackay, *Amer. Chem. Journ.*, **19**. 98, 1897 ; M. A. Graham, *ib.*, **48**. 145, 1912 ; T. Dreisch, *Zeit. Physik*, **40**. 714, 1927 ; P. Walden, *Zeit. phys. Chem.*, **1**. 541, 1887 ; T. W. Richards and F. Bonnet, *ib.*, **47**. 29, 1904 ; *Proc. Amer. Acad.*, **39**. 26, 1903 ; O. Knoblauch, *Wied. Ann.*, **43**. 738, 1891 ; M. Krüger, *Pogg. Ann.*, **61**. 218, 1844 ; W. N. Hartley, *Trans. Roy. Dublin Soc.*, (2), **7**. 253, 1900 ; E. Stiasny, *Gerber.*, **33**. 124, 1907 ; *Zeit. angew. Chem.*, **37**. 913, 1924 ; E. Stiasny, K. Lochmann, and E. Mezey, *Collegium*, 190, 1925 ; E. Stiasny and K. Lochmann, *ib.*, 200, 1925 ; E. Stiasny and L. Szego, *ib.*, 41, 1926 ; E. Stiasny and D. Balanyi, *ib.*, 86, 1927 ; 72, 1928 ; E. Stiasny and O. Grimm, *ib.*, 49, 1928 ; K. Friedrich, *Met.*, **7**. 323, 1910 ; F. S. Williamson, *Journ. Phys. Chem.*, **27**. 384, 1923 ; B. Cabrera and M. Marquina, *Ann. Fis. Quim.*, **15**. 199, 1917 ; B. Cabrera and S. P. de Rubies, *ib.*, **17**. 149, 1919 ; **20**. 509, 1922 ; J. M. Hiebendaal, *Onderzoek over eenige Absorptiespectra*, Utrecht, 1873 ; W. Böhlendorff, *Studien zur Absorptionsspectralanalyse*, Erlangen, 1890 ; D. Brewster, *Phil. Mag.*, (4), **24**. 441, 1862 ; O. Liebknecht and A. P. Wills, *Ann. Physik*, (4), **1**. 178, 1900 ; G. Jäger and S. Meyer, *Wied. Ann.*, **67**. 427, 707, 1899 ; *Sitzber. Akad. Wien*, **106**. 594, 623, 1897 ; **107**. 5, 1898 ; F. Hans, *Zeit. anorg. Chem.*, **140**. 337, 1824 ; F. Feigl, *ib.*, **119**. 305, 1922 ; F. Krauss, H. Querengässer and P. Weyer, *ib.*, **179**. 413, 1929 ; O. Grimm, *Eigenschaften und Verhalten verschieden vorbehandelter Chromchlorid- und Chromsulfat-Lösungen*, Darmstadt, 1927 ; W. R. Hodgkinson and C. C. Trench, *B.A. Rep.*, 675, 1892 ; *Chem. News*, **66**. 223, 1892 ; N. Demassieux and J. Heyrovsky, *Journ. Chim. Phys.*, **26**. 219, 1929 ; G. Fuseya, K. Murata and R. Yumoto, *Tech. Rep. Tohoku Univ.*, **9**. 33, 1930 ; K. Flick, *Trennung von Metallen durch auswählende Dissoziation von Salzen in Gemischen*, Mainz, 1929 ; P. Philipp, *Untersuchungen über Magnetisierungszahlen von Salzen der Eisengrüppe und ihre Abhängigkeit von der Konzentration*, Rostock, 1914 ; W. Manchot, M. Jahrstorfer and H. Zepter, *Zeit. anorg. Chem.*, **141**. 45, 1924 ; R. Reinicke, *ib.*, **187**. 49, 1930 ; E. Wydler, *French Pat. No.* 685118, 1929 ; E. Moles and M. Crespi, *Zeit. phys. Chem.*, **130**. 337, 1927 ; T. Ishiwara, *Science Rep. Tohoku Univ.*, **3**. 303, 1914 ; K. Honda and T. Ishiwara, *ib.*, **4**, 215, 1915.

[3] W. Ipatieff and A. Kisseleff, *Ber.*, **59**. B, 1418, 1926 ; *Journ. Russ. Phys. Chem. Soc.*, **58**. 664, 686, 692, 698, 1926 ; J. L. Gay Lussac, *Ann. Chim. Phys.*, (2), **16**. 102, 1821 ; J. Fritzsche, *Mem. Acad. St. Petersburg*, **6**. 181, 1840 ; *Journ. prakt. Chem.*, (1), **19**. 176, 1840 ; *Pogg. Ann.*, **50**. 540, 1840 ; A. Schrötter, *ib.*, **59**. 616, 1843 ; P. Plantamour, *Berzelius' Jahresber.*, **20**. ii, 101, 1840 ; A. Pictet and G. Karl, *Bull. Soc. Chim.*, (4), **3**. 1114, 1908 ; *Arch. Sciences Genève*, (4), **26**. 437, 1908 ; P. A. Bolley, *Journ. Pharm. Chim.*, (1), **9**. 226, 1846 ; *Liebig's Ann.*, **56**. 113, 1845 ; H. Schiff, *ib.*, **126**. 165, 1863 ; L. F. Gilbert, H. Buckley and I. Marson, *Journ. Chem. Soc.*, **121**. 1934, 1922 ; D. N. Tarassenkoff, *Arb. Russ. Inst. Pure Chem. Reagents*, **6**, 1927 ; A. W. Rakowsky and D. N. Tarassenkoff, *Zeit. anorg. Chem.*, **174**. 91, 1928 ; J. Meyer and V. Stateczny, *ib.*, **122**. 1, 1922 ; V. Stateczny, *Ueber einige Polysäuren von Elementen der Schwefelgruppe*, Breslau, 1922 ; B. Cabrera and S. P. de Rubies, *Anal. Fis. Quim*, **20**. 175, 1922.

§ 30. The Complex Salts of Chromic Sulphates

The most important complex sulphates are the chrome-alums in which tervalent chromium replaces aluminium in the ordinary alums, so that the general formula for the series is $R'_2SO_4.Cr_2(SO_4)_3.24H_2O$, or $R'Cr(SO_4)_2.12H_2O$. A. Mitscherlich[1] prepared **ammonium chromium sulphate,** or **ammonium disulphatochromiate,** $(NH_4)_2SO_4.Cr_2(SO_4)_3.24H_2O$, or $(NH_4)Cr(SO_4)_2.12H_2O$, by mixing a sulphuric acid soln. of violet chromic sulphate with ammonia; A. Schrötter, by adding ammonium sulphate to a conc. soln. of violet chromic sulphate when crystals of the ammonium chrome-alum are precipitated, and J. L. Howe and E. A. O'Neal, by the electrolysis of a soln. of ammonium chromate in sulphuric acid—this salt collects at the negative pole. J. Hertkorn prepared it as in the case of the potassium salt—*vide infra.* A. Mitscherlich found that the crystals are regular octahedra, with surfaces of cubes and dodecahedra. The cleavage on the octahedral face is indistinct. T. Klobb prepared solid soln. of ammonium chromic alum with ammonium ferric and with ammonium aluminium alums. W. Haidinger found the crystals to be violet-blue passing into columbine-red; and, added A. Schrötter, they are ruby-red by transmitted light. They are moderately transparent, and have a sweetish saline taste. A. Schrötter gave 1·736 for the sp. gr. at 21°; O. Pettersson, 1·728 at 20°; and J. H. Gladstone, 1·719. G. T. Gerlach found the sp. gr. of violet soln. containing 2·195, 4·390, and 6·585 per cent. $(NH_4)Cr(SO_4)_2$ are respectively 1·0200, 1·0405, and 1·0610 at 15°/15°; and with green soln. at 15°/15°,

$(NH_4)Cr(SO_4)_2$	5·487	10·974	16·461	27·435	38·409	49·383 per cent.
Sp. gr. . .	1·044	1·091	1·142	1·255	1·384	1·532

The sp. gr. of the sat. violet soln. is 1·070 at 15°/15°. P. A. Favre and C. A. Valson studied the change in vol. which occurs when this alum passes into soln. H. C. Jones and E. Mackay found the lowerings of the f.p. produced by ammonium chrome alum for 0·097, 0·0484, and 0·0291 per cent. soln. are, respectively, 7·92, 8·26, and 9·14, and these values are about 0·8 less than the sum of the values of the constituents. This means that the f.p. of the soln. confirm the evidence from the conductivity data, that alum molecules exist to some extent in the more conc. soln. According to A. Schrötter, the salt effloresces superficially in air, and becomes covered with a pearl-grey powder. The m.p. is 100°. J. Locke gave 94° for the m.p. A. Schrötter observed that three-fourths of the water of crystallization is evolved when the salt melts, and the liquid shows no signs of dichroism; it solidifies to a pale green mass which gives off its remaining water above 300°. G. D. van Cleeff said that half its combined water is lost over sulphuric acid, and at 100°, five-sixths is given off. F. Ephraim and P. Wagner found that the vap. press., p mm., of the salt is:

	50°	60·5°	72°	80°	80·5°	86°
p . .	40	80	162	244	260	326 mm.

H. C. Jones and E. Mackay found that the f.p. of soln. with 92·740, 27·822, and 5·564 grms. of $(NH_4)Cr(SO_4)_2.12H_2O$ per litre are, respectively, 0·768°, —0·266°, and —0·064°. P. A. Favre and C. A. Valson gave for the heat of soln. of a mol of the sulphate —9·628 Cals. at 8° to 10°; and —9·889 Cals. at 19° to 21°. They also found for the heat of precipitation of a fresh violet soln. of a mol of ammonium chrome-alum, 14·636 Cals., and after the lapse of 14 days, 13·9 Cals. The corresponding value for a green soln. is 7·641 Cals. C. Soret gave for the index of refraction, μ, between 7° and 14°, for light of different wave-lengths, λ,

λ .	*G*-line	*F*-line	*B*-line	*E*-line	*D*-line	*C*-line	*B*-line	*A*-line
μ .	1·49594	1·49040	1·48794	1·48744	1·48418	1·48125	1·48014	1·47911

J. H. Gladstone gave $(\mu-1)/D=0·2781$ for the sp. refraction for the A-line; and $(\mu_A-\mu_G)/D=0·0104$ for the sp. dispersion. J. M. Hiebendaal, and H. Sauer studied the absorption spectrum of ammonium chrome-alum.

H. C. Jones and E. Mackay measured the mol. electrical conductivity, μ mhos, of the violet soln.; and H. H. Hosford and H. C. Jones gave for soln. with a mol of the violet salt in v litres between 0° and 35°, and S. F. Howard and H. C. Jones, between 35° and 65°,

v		8	16	32	128	512	1024	2048	4096
μ	0°	82·4	94·6	107·1	137·6	176·0	198·8	—	259·0
	12·5°	113·1	181·0	149·1	194·5	253·0	289·3	—	378·0
	25°	145·9	169·6	193·8	255·7	341·2	395·3	—	523·5
	35°	169·8	197·9	228·6	302·7	410·2	483·1	577·4	671·2
	65°	245·0	288·8	333·5	459·1	649·0	754·8	897·3	1050·3
α	35°	25·3	29·5	34·1	45·1	61·1	72·0	86·0	100·0
	65°	23·3	27·5	31·7	43·7	61·8	71·9	85·4	100·0

The values at the higher temp. are of course affected by the presence of x per cent. of the green salt. α refers to the calculated percentage ionization. The corresponding values for green soln. were:

v		8	16	32	128	512	1024	2048	4096
μ	0°	103·6	119·7	136·4	172·3	202·6	215·6	222·0	234·4
	12·5°	133·2	155·4	178·2	228·4	274·4	294·2	313·5	328·4
	25°	162·9	190·6	220·8	288·1	355·7	386·2	414·0	458·1
	35°	194·0	229·8	268·0	355·6	446·1	492·2	537·1	589·8
	65°	250·7	299·6	352·2	489·8	673·8	789·6	924·3	1061·7
α	35°	32·9	39·0	45·4	60·3	75·6	83·4	91·1	100·0
	65°	23·6	28·3	33·2	46·1	63·5	74·4	87·1	100·0

According to A. Schrötter, ammonium chrome-alum dissolves in cold water forming a bluish-violet soln. Alcohol precipitates the alum from its violet soln. At about 75° or 80°, the bluish-violet aq. soln. assumes a grass-green colour owing to some molecular change, so that the soln. on evaporation does not yield crystals, but dries to a green mass; nor does the green soln. give a precipitate with alcohol, but it either mixes with it, or forms a substratum with the alcohol floating on the surface. If the green soln. is diluted with water, and left to stand for ten days, the violet alum is gradually reproduced. When a soln. of the violet alum is mixed with an excess of sulphuric acid, then treated with alcohol, the green soln. decanted from the precipitated blue salt, and mixed with so much ammonia that it still remains slightly acid, a dark green, highly acid soln. settles to the bottom. When this soln. is allowed to stand for a long time, it decolorizes, and a light green salt is deposited. It has the composition $14(NH_4)_2SO_4.Cr_2(SO_4)_3.3H_2SO_4.33H_2O$. J. Locke found that at 25° a litre of water dissolves 212·1 grms. of $(NH_4)Cr(SO_4)_2.12H_2O$, or 107·8 grms., *i.e.* 9·75 per cent. of $(NH_4)Cr(SO_4)_2$. As in the case of the chromium salts previously discussed, the soln. of the violet salt in water involves a state of equilibrium between the green and the violet forms, and this is dependent on the temp. The time required for equilibrium is represented by the following observations of I. Koppel on the solubilities, S grams of $(NH_4)Cr(SO_4)_2$ per 100 grms. of soln., after the lapse of the stated intervals of time:

Time		2·5	20	50	100	200	300	400	∞ hrs.
S	0°	3·82	3·68	3·73	—	—	—	—	3·77
	30°	10·6	11·9	13·12	16·25	15·2	15·7	16·0	16·00
	40°	15·5	19·3	21·6	22·8	24·5	—	24·8	24·70

He inferred from conductivity and f.p. determinations that at 0° a sat. soln. of the violet alum has 3·8 per cent. of $(NH_4)Cr(SO_4)_2$; and at 40°, after the elapse of 20 days the same soln. is in equilibrium when about 52 per cent. of the solute is in the violet form and 48 per cent. in the green form; while at 55°, equilibrium occurs when 39 per cent. of violet alum and 61 per cent. of green alum are present. Similar data were obtained with conc. soln. The calculations assume that only one variety of the green salt is produced.

Anhydrous or dehydrated ammonium chrome-alum was obtained by M. Traube by melting chromic oxide or a chromic salt with an excess of ammonium sulphate. It was also prepared by T. Klobb—*vide infra,* the ammonium trisulphatochromiate. The salt appears in hexagonal plates, or as a pale green powder which, according to P. A. Favre and C. A. Valson, had a sp. gr. of 2·472 at 21·9°. M. Traube found that the salt does not melt nor yet decompose at 350°. It reddens when heated. It is insoluble in cold water; and it is not attacked by boiling water, dil. boiling alkali-lye, or acids, or by conc. hydrochloric acid. T. Klobb said that it is isomorphous with the dehydrated potash-alum and soda-alums and with the corresponding aluminium and ferric salts. A. Recoura obtained what he regarded as a pentahydrate, by dehydrating ammonium chrome-alum.

W. Meyeringh obtained **hydroxylamine chromium sulphate,** or **hydroxylamine disulphatochromiate,** $(NH_3OH)_2SO_4.Cr_2(SO_4)_3.24H_2O$, or $(NH_3OH)Cr(SO_4)_2.12H_2O$, in cubic crystals, from a soln. of the component salts. H. Sauer studied the absorption spectrum of this salt and of the methylamine. F. Sommer and K. Weise prepared **hydrazine chromium sulphate,** or **hydrazinium disulphatochromiate,** $(N_2H_5)Cr(SO_4)_2.12H_2O$, which furnishes dark violet octahedral crystals, freely soluble in water. G. Canneri prepared **guanidine disulphatochromiate,** $(C_6H_5N_3)_2.H_2SO_4.Cr_2(SO_4)_3.12H_2O$; it is isomorphous with the corresponding sulphatodialuminate.

A. Schrötter prepared **sodium chromium sulphate,** or **sodium disulphatochromiate,** $Na_2SO_4.Cr_2(SO_4)_3.24H_2O$, or $NaCr(SO_4)_2.12H_2O$, by gradually mixing a mol of sodium dichromate with 3 mols of conc. sulphuric acid so as to avoid much heating; adding alcohol, and then allowing the soln. to stand. Definite crystals were not obtained. E. I. Orloff prepared the salt in crystals by the following process:

> Add 100 grms. of xylene, in small portions at a time and with constant stirring, to a sealed flask containing 300 grms. of sulphuric acid of sp. gr. 1·84; when the xylene has dissolved, add 295 grms. more of the acid, and pour the mixture into a large porcelain dish containing a litre of water, and add 375 grms. of finely powdered sodium dichromate in small portions at a time. The reduction takes place in the cold, and it is completed by warming the liquid which then turns green. The soln. is then evaporated to 1339 grms., and the product poured into flat porcelain dishes, covered, and left to crystallize at room temp. The small crystals can be recrystallized from water by slowly evaporating sat. soln.

A. Schrötter found that the salt loses 16 mols. of water at 100°; and it weathers more rapidly in air than the ammonium or potassium salt. F. Ephraim and P. Wagner found the vap. press., p mm., of the hydrate to be:

	51°	63°	71°	76°	80°	82·5°	90°
p . .	43	83	122	162	241	250	382 mm.

T. Klobb obtained mixed crystals of the anhydrous sodium and ammonium chromium sulphates, $(NH_4,Na)SO_4.Cr_2(SO_4)_3$, by melting together chromic sulphate or chrome-alum with ammonium and sodium sulphates. The hexagonal crystals are isomorphous with the anhydrous alums. A. N. Bach found the transition temp. to be between 60° and 70°.

Crystals of potassium chrome-alum, **potassium chromium sulphate,** or **potassium disulphatochromiate,** $K_2SO_4.Cr_2(SO_4)_3.24H_2O$, or $KCr(SO_4)_2.12H_2O$, were first obtained by A. Mussin-Puschkin; and J. J. Berzelius obtained the violet crystals by the spontaneous evaporation of a soln. of a mixture of the component salts. A. Schrötter, and F. A. Rohrman and N. W. Taylor obtained it by sat. with sulphur dioxide a sat. soln. of potassium dichromate and conc. sulphuric acid prepared in the cold; N. W. Fischer, M. Traube, and H. Löwel used a modification of the process with alcohol as reducing agent; A. Lielegg used oxalic acid as reducing agent, and, added E. A. Werner, if too little water be present, a complex oxalate is formed. G. Städeler obtained chrome-alum as a by-product in the preparation of acetaldehyde. The manufacture of chrome-alum was described by P. Hasenclever, etc.—*vide supra,* the extraction of chromium. J. Hertkorn obtained it by treating a soln. of chromic sulphate in water or sulphuric acid with potassium sulphite or hydrosulphite—with or without the addition of a little nitrate or nitrite, and then subjecting it to the action of sulphur dioxide under ordinary and an increased press. H. C. Starck described the preparation of a soln. from ferrochromium, where the sulphuric acid soln. of the alloy is treated with potassium dichromate, heated to the b.p. at atm. press., preferably with the addition of sodium carbonate, or at a higher press. The iron compounds are thus precipitated, and the filtered soln. is treated with potassium sulphate for chrome alum. Processes were also described by A. W. Gregory, and O. Nydegger. H. Chaumat prepared the salt by the electrolysis of a soln. of potassium dichromate mixed with sulphuric acid. The liquor is circulated in the cathode compartment, which is separated from the anode by a porous vessel, the cathode preferably consisting of graphite powder packed round a carbon core. Dil. sulphuric acid is circulated in the anode compartment, and to utilize the SO_3-ion, which is disengaged at the anode, the latter may take the form of a copper electrode surrounded by copper shavings, whereby copper sulphate is formed in the course of electrolysis. A. Stiassny, H. N. Warren, F. A. Rohrman and N. W. Taylor, and A. Polis discussed the formation of large crystals of the salt. E. S. Hedges and J. E. Myers studied the periodic crystallization of this salt. Analyses were made by N. W. Fischer, and P. de Boissieu. E. J. Maumené found that the analyses indicated between 23·9 and 24·1 mols. of water, and V. A. Jacquelain, 22 mols.—but this number probably refers to the partly effloresced salt. T. Ishikawa studied the reciprocal salt pair $\{K_2,(NH_4)_2\}-\{(SO_4),(CrO_4)\}$ at 25° ; and A. Fock, and G. Tammann and A. Sworykin, isomorphous mixtures with potash-alum. R. Hollmann's observations on the composition of the solid soln. and mother-liquor for potassium chromium and potassium aluminium alums are summarized in Fig. 81, and his observations on the vap. press. of the solid soln. in Fig. 82. There are two minima, and one maximum in the curve.

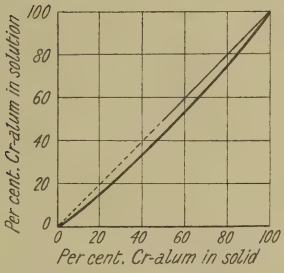


FIG. 81.—Composition of Solution and Solid Mixtures of Potassium Chromium and Potassium Aluminium Alums.

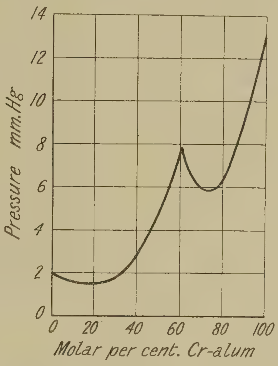


FIG. 82.—Vapour Pressures of Mixtures of Potassium Chromium in Potassium Aluminium Alums.

The octahedral, cubic crystals are violet to black in colour, and appear ruby-red in thin layers ; and J. H. Kastle found that the intensity of the colour is very much reduced at liquid air temp. F. Klocke, C. F. Rammelsberg, C. von Hauer, and J. W. Retgers showed that the crystals are isomorphous with other alums, for they show similar corrosion figures. E. Dittler obtained overgrowth with potassium aluminium sulphate. T. V. Barker found a close connection between parallel overgrowths in chrome-alum, potash-alum, and ammonia-alum and the mol. vols which are respectively 542·2, 541·6, and 552·2. C. von Hauer found that with the introduction of a crystal of iron-alum in a sat. soln. of chrome-alum nearly all the latter separates out ; while L. de Boisbaudran found that a sat. soln. of basic ammonium aluminium alum does not affect the octahedral faces of the crystal, but the cubic faces are slowly attacked. K. Grinakowsky found that different faces of the crystal do not all possess the same solubilities, and that the degree of supersaturation has different values for the different faces of the polyhedron, and is dependent on the temp. At low temp., the edges and angles are the less soluble; and at high temp., the faces; the edges of obtuse angles are more stable than the summits of four-faced angles at low temp., whilst at high temp. the reverse applies. P. N. Pawloff's statement, that the surface layer of a crystalline substance is vectorial in character and influences the direction and general course of the deformation, applies to some extent, especially in the case of twinning deformation. The latter indicates the existence of a temperature-limit for a possible equilibrium of the system crystal-mother liquor, the surface energy being, for a given crystallographic form, a maximum. The direction and course of the deformation of crystals of chrome-alum show that the octahedron is the most stable form, and is followed in order by the rhombic dodecahedron, cube, and trapezohedron. The crystals were studied by E. S. von Fedoroff.

L. Vegard and H. Schjelderup obtained X-radiograms of the alums, and deduced probable arrangements for the metal, sulphur, and oxygen atoms in the space-lattice. They added that the crystal model divides the 24 mols. of water into six groups, which groups are cubically disposed with reference to the four tetrahedrally arranged atoms of sulphur. The model makes no distinction between the water of crystallization and the other constituents of the alum. Any hypothesis which would distinguish the water of crystallization from water of constitution could not be reconciled with the observed relations between the high-frequency reflection spectra. The removal of the water of crystallization is necessarily accompanied by the destruction of that structure which is characteristic of the hydrated salt. The unit hexagonal cells of the anhydrous salt furnished $a=4{\cdot}737$ A., and $c=8{\cdot}030$ A., and each unit cell contains one mol. of $KCr(SO_4)_2$. J. M. Cork found that the unit cubic cell has $a=12{\cdot}20$ A., and that there are four mols. per cell. The eight metal atoms take positions at the corners, centre, centre of faces, and mid-points of the edges of the cell making a rock salt arrangement of the univalent and tervalent metals. C. Schaefer and M. Schubert, L. Vegard and E. Esp, L. Vegard and A. Maurstad, and L. Vegard discussed this subject.

H. Schiff found the sp. gr. to be 1·845; L. Playfair and J. P. Joule, 1·856; H. Kopp, 1·848; J. Dewar, 1·834 at −188°, and 1·82 at 17°; O. Pettersson, 1·842 at 20·8°; J. H. Gladstone, 1·817; while W. Spring gave

	0°	10°	20°	30°	40°	50°	60°
Sp. gr. .	1·8308	1·8282	1·8278	1·8274	1·8269	1·8259	1·8202

According to E. Moles and M. Crespi, the sp. gr. and mol. vol., at 25°/4°, of $KCr(SO_4)_2$ are 2·548 and 111 respectively; of $KCr(SO_4)_2.H_2O$, respectively 2·482 and 120; of $K[Cr(H_2O)_6](SO_4)_2$, respectively 2·17 and 180; and of $K[Cr(H_2O)_6](SO_4)_2.6H_2O$, 1·834 and 272. B. Franz found the sp. gr. of soln. with the following number of grams of $KCr(SO_4)_2.12H_2O$ per 100 grms. of soln., to be at 17·5°,

Salt .	5	10	20	30	40	50	60	70 per cent.
Sp. gr. .	1·0174	1·0342	1·0746	1·1274	1·1896	1·2894	1·4566	1·6362

while G. T. Gerlach gave for violet soln. with 2·84, 5·68, and 8·52 per cent. of the anhydrous salt, respectively 1·0275, 1·055, and 1·0835 at 15°/15°; and for the green soln.:

$KCr(SO_4)_2$	5·68	11·36	17·03	22·71	28·39	34·07	39·74	45·42	51·10
Sp. gr. .	1·050	1·103	1·161	1·225	1·295	1·371	1·453	1·451	1·635

so that the sp. gr. of the violet soln. is greater than is the case with the green soln. M. A. Rakuzin and co-workers found that a sat. soln. of the green alum has 114·19 parts of salt per 100 parts of water at 20°, and the sp. gr. of the sat. soln. is 1·6683. For a concentration C per cent.,

C	5	10	20	40	60	80	100	114·19 per cent.
Sp. gr.	1·0378	1·0641	1·1076	1·1623	1·2531	1·3524	1·4404	1·6683

The sp. gr. of the soln. does not increase proportionally with concentration, and soln. of the same conc. made with different samples of alum have different sp. gr. This is attributed to differences in the relative proportions of the green and violet salts in the different soln. K. Grinakowsky found a transition temp. at 78°; and C. Montemartini and L. Losana, at 77°. P. A. Favre and C. A. Valson, and G. Beck studied the vol. changes which occur when the alum dissolves. J. Beckenkamp found the elastic modulus of the crystals perpendicular to the cubic surface to be 1608 kgrms. per sq. mm.; perpendicular to the dodecahedral surface, 1771 kgrms. per sq. mm.; and perpendicular to the octahedral surface, 1832 kgrms. per sq. mm. A. Ferrero observed that for a 13·75 per cent. soln., at 20·5°, the viscosity is 0·01261 G.G.S. units for the violet soln., and 0·1185 for the green soln. prepared at 80°; similarly for a 20·5 per cent. soln. at 20·5°, 0·01417 for the violet soln. and 0·01294 for the green soln. prepared at 80°. The difference between the green and violet soln. decreases with increasing dilution. R. F. d'Arcy made observations on this subject. F. Rüdorff found that in dil. soln., the potassium sulphate diffuses more rapidly than the chromium sulphate; and D. M. Torrance and N. Knight, G. D. van Cleeff, and M. E. Dougal observed that in the dialysis of the green soln., more sulphuric acid passes through the membrane than is the case with the violet soln. C. Montemartini and L. Losana studied the viscosity of the soln. P. W. Bridgman gave for the compressibility of chrome-alum at 30°, $-\delta v/v_0=64{\cdot}86\times10^{-7}p-112{\cdot}5\times10^{-12}p^2$.

W. Spring gave for the thermal expansion the linear coeff. $0{\cdot}0_4246$ between 0° and 60°. H. Kopp found the sp. ht. to be 0·324. A. Eucken and G. Kuhn found the sp. ht. at −190° to be 0·00242, and the value at 0°, 0·00426. According to C. Pape, the crystals are stable in air; but uninjured crystals effloresce at 29°. N. W. Fischer added that when the salt is impure it will effloresce on the surface when exposed to air, and, if chromic sulphate be in excess, it will assume a green colour, and a violet colour if the potassium sulphate predominates. G. D. van Cleeff, and J. Juttke observed that the salt loses 12 to 13 mols. of water when confined over sulphuric acid, in vacuo; and H. Löwel added that a similar amount is lost over quicklime, or conc. sulphuric acid, at 25° to 30°, and no more is lost by the granular mass at 80° to 90°; at 100° or over, it loses more water and becomes green. J. Juttke observed that all the water can be expelled at 100° without the alum becoming insoluble or decomposing; and G. D. van Cleeff observed a loss of 21 mols. of water at 110°. W. Müller-Erzbach found that at 0·49 mm. press. and 27·8°, half the water of crystallization is given off, and the residue when kept 7 days at 30° loses very little more water. For the dissociation press., p mm. in the reaction: $KCr(SO_4)_2.12H_2O \rightleftharpoons KCr(SO_4)_2.6H_2O+6H_2O$, H. Lescœur and D. Mathurin observed p=3·7 at 10°; 6·0 at 15°; 9·1 at 20°; 12·3 at 25°; 16·7 at 30°; and 23·8 at 35°; while F. Ephraim and P. Wagner gave

	31°	40°	50°	55°	60°	70°	73°	77·5°	79°
p	15	31	63	86	119	202	224	250	260

R. Hollmann gave p=13·2 mm. at 17° to 19°; and he also obtained values for solid soln. of the chromium and aluminium alums. H. Lescœur and D. Mathurin found that over conc. sulphuric acid the alum loses half its water of crystallization and passes into a lilac-coloured powder which does not lose its colour at 75°. At 20°, the dissociation press., p mm. of the moist alum, $KCr(SO_4)_2 : nH_2O$, is 15·25 mm. for n=13·05, and 15·0 for n=12·3; for n=12·1, p=9·8, and the violet powder produced when n=11·8, has p=9·1. This value of p remains approximately constant up to n=6·01. When n=5·72, a lilac powder is formed with p=3·2, and for n=5·4, p=3·2. When n=3·92, p is less than 1·5; and when n=2·35, p is less than 1·0. The n=6-hydrate was found by A. Recoura to lose no water between 80° and 90°, but at 110° it gives off 4 mols. and becomes green. A. Beutel found that the velocity with which water is expelled is accelerated by exposing the crystals to visible and ultra-violet light. Observations on the dissociation of the alums were also made by E. J. Maumené, and P. de Boissieu. When the salt is heated to 200°, N. W. Fischer, and C. Hertwig found that 22 mols. of water are given off, and the remainder between 300° and 400°. E. Moles and M. Crespi found that the salt $K[Cr(H_2O)_6](SO_4)_2.6H_2O$ loses about 5·9 mols. of water at 18°, and at 60°; while $K[Cr(H_2O)_6](SO_4)_2$ loses 5·30 mols. of water at 140°; and $KCr(SO_4)_2.H_2O$ loses 0·9 mol. at 350°. According to H. Löwel, when the salt is gradually heated between 300° and 350° it furnishes the anhydrous soluble salt; but over 350°, without losing much weight, it forms the yellowish-green insoluble salt. F. Krauss and co-workers' observations on the effect of heat on potash-chrome-alum can be represented by Fig. 83. The anhydrous salt begins to lose sulphur trioxide at 612°.

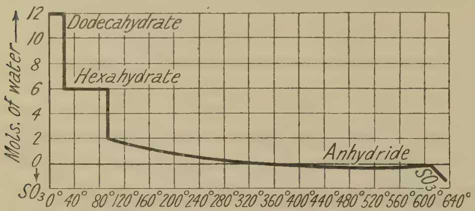


FIG. 83.—The Action of Heat on Potassium Chrome-alum.

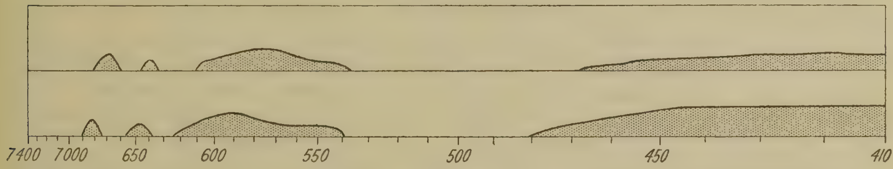
The salt melts in its water of crystallization at 80° to 90°. W. A. Tilden, and J. Locke gave 89° for the m.p. H. C. Jones and E. Mackay found for the f.p. of soln. of 117·44, 29·36, and 5·872 grms. of $KCr(SO_4)_2.12H_2O$ in a litre of water, the respective values —0·888°, —0·267°, and —0·065°.

J. Thomsen found the heat of soln. for a mol of $KCr(SO_4)_2.12H_2O$ to be —9·564 Cals. at 8° to 11°; and P. A. Favre and C. A. Valson, —9·651 Cals. at 8° to 11°; and —9·499 Cals. at 19° to 21°. Conc. soln. were found to give almost the same numbers, but the partially dehydrated salt gave 3·825 Cals. H. Löwel, and W. R. Whitney found that barium chloride precipitates all the sulphate from the violet soln. in the cold; and P. A. Favre and C. A. Valson observed that for a mol of $KCr(SO_4)_2$, the heat of precipitation is 14·767 Cals. The heat required for precipitation of the first half of the SO_4 is 7·514 Cals., and for the second half, 7·388 Cals.; similarly, for successive quarters, the heats of precipitation are respectively 3·680, 3·702, 3·665, and 3·699 Cals. P. A. Favre and C. A. Valson, and W. R. Whitney found that only half the sulphate is precipitated at once from the green, modified soln. The total heat of precipitation was found by P. A. Favre and C. A. Valson to be 8·251 Cals. per mol of $KCr(SO_4)_2$, and for the first and second halves 8·142 Cals and 0·204 Cals. respectively; while for the first, second, and third quarters, the values were 4·104 Cals., 4·102 Cals., and 0·146 Cal. respectively. The heat of precipitation for $\frac{1}{2}K_2SO_4$ is 3·3 Cals.; for $\frac{1}{2}Cr_2(SO_4)_3$, 4·9 Cals.; and for $\frac{1}{2}H_2SO_4$, 5·053 Cals. This shows that only half the contained sulphate is precipitable at once by barium chloride from a freshly prepared soln. of the salt.

C. Soret observed that the index of refraction, μ, at 0° to 17°, for light of different wave-lengths, λ, is:

λ .	*G*-line	*F*-line	*b*-line	*E*-line	*D*-line	*C*-line	*B*-line	*A*-line
μ .	1·49309	1·48753	1·48513	1·48459	1·48137	1·47805	1·47738	1·47642

C. Soret and co-workers found that refractive indices of the green soln. to be less than those of violet soln. J. H. Gladstone gave for the sp. refraction for the *A*-line, $(\mu-1)/D$=0·2616; and for the sp. dispersion $(\mu_A-\mu_G)/D$=0·0098. J. Formanek observed that the absorption spectrum of the violet soln., Fig. 84, has a weak band at 671·8, and a stronger one between 610 and 540 with a maximum at 578; at 470, the absorption of short waves begins; J. M. Hiebendaal observed a weak band at 658, and a stronger one between 590 and 535; A. Étard found bands between 678 and 670, and between 654 and 633. O. Knoblauch observed a band between 610 and 558; and W. Böhlendorff, strips at 672, and 640, and a band between 609 and 568. Observations were also made by W. N. Hartley, H. Sauer, G. D. Liveing and J. Dewar, and K. Vierordt. H. W. Vogel found with a violet soln., a strong line at 665, a feebler one at 656, and a broad band with a maximum at 589, and an absorption in the violet begins at 489. The solid salt does not show the first line, and the band is more towards the red. J. Formanek found that the green soln. has a strip at 681, and a second one at 640 which is connected with a band extending as far as 540 with a maximum at 591. The absorption in the violet begins at 480, Fig. 85. J. M. Hiebandaal found with thick layers of soln. a band between 660 and 523, and an absorption beginning at 469; with thinner layers of soln., there are bands between 673 and 667, and between 632 and 544; while with still thinner layers, there is a band between 613 and 535. Observations were also made by W. N. Hartley, and W. Böhlendorff. H. W. Vogel found a small strip at 686, and a band between 656 and 530, while absorption begins at 486. The solid salt, and the alcoholic soln. have different spectra. H. C. Jones and W. W. Strong, K. Grinakowsky, and A. Byk and H. Jaffe studied the violet and ultra-violet spectra of the soln.; H. Sauer, the absorption spectrum. S. Higuchi, the ultra-red spectrum; and H. du Bois and G. J. Elias, the influence of magnetization and temp. on the spectra of the solid salts. H. M. Vernon estimated the ionization from the colour of aq. soln. M. Bamberger and R. Grengg found that the colour fades as the temp. approaches —190°. C. Doelter observed that radium radiations change the crystals into a pale violet powder.



Figs. 84 and 85.—Absorption Spectra of Solutions of Potassium Chrome-Alum.

H. C. Jones and E. Mackay, K. Grinakowsky, F. Schmidt, and F. S. Svenson measured the electrical conductivity, μ mhos, of soln. of the salt; H. H. Hosford and H. C. Jones obtained the accompanying values between 0° and 35°, and S. F. Howard and H. C. Jones between 35° and 65°, for violet soln. containing a mol of $KCr(SO_4)_2.12H_2O$ in v litres. The computed values for the percentage degree of ionization, α, are affected by the formation of x per cent. of the green salt.

v		8	16	32	128	512	1024	2048	4096
μ	0°	75·8	87·3	99·0	127·0	161·1	186·6	212·3	245·8
	12·5°	105·0	121·2	138·1	179·5	232·0	271·6	314·2	364·8
	25°	135·3	157·3	179·6	236·7	311·5	369·6	428·8	500·1
	35°	167·0	183·3	225·8	288·1	404·1	465·4	546·9	637·4
	65°	242·0	276·7	339·9	467·3	658·9	785·4	928·4	1083·0
α	35°	26·20	28·75	35·42	46·77	63·40	73·02	85·80	100·0
	65°	22·35	25·55	31·39	43·15	60·84	72·52	85·73	100·0

V. Monti found that the conductivity of the green soln. is greater than that of the violet soln. H. C. Jones and E. Mackay found that the change from violet to green corresponds with the change in the conductivity of the soln. H. H. Hosford and H. C. Jones, and S. F. Howard and H. C. Jones, obtained the following results for green soln. for the temp. indicated in connection with the violet soln. :

v		8	16	32	128	512	1024	2048	4096
μ	0°	107·4	126·8	146·5	188·9	224·2	244·4	—	290·2
	12·5°	138·2	163·7	190·5	249·1	301·4	330·6	—	402·8
	25°	168·4	199·9	233·3	308·9	381·6	425·2	—	531·5
	35°	194·0	219·2	270·4	358·0	474·9	487·6	535·9	584·3
	65°	248·1	279·3	352·6	486·0	699·3	771·9	903·3	1017·0
a	35°	33·20	37·51	46·27	61·27	81·28	83·45	91·72	100·0
	65°	24·39	27·47	34·67	47·78	68·76	75·90	88·81	100·0

H. T. S. Britton found that, at 18°, a 0·0050*N*- and 0·0067*N*-soln. of the violet and green salts have respectively an e.m.f. of 0·467 and 0·395 volt against a *N*-calomel electrode ; the $H^{\cdot}$-ion concentrations are $p_H=3·19$ and 1·94 ; and the percentage hydrolysis is 2·16 and 28·7. In the electrometric titration with sodium hydroxide, precipitation began with the e.m.f. respectively 0·591 and 0·587 volt, when the $H^{\cdot}$-ion conc. was $p_H=5·30$ and 5·27 ; or when 1·00 and 1·21 eq. of alkali per eq. Cr had been added ; and precipitation was complete when 2·75 and 2·71 eq. of alkali had been added. F. L. S. Jones studied the formation of complex anions in soln.—*vide supra*, chromic sulphate. According to N. Demassieux and J. Heyrovsky, the polarization curves obtained in the electrolysis of tervalent chromium soln. show inflexions corresponding with either $Cr^{\cdots}\rightarrow Cr^{\cdot\cdot}+\oplus$ or $Cr^{\cdots}\rightarrow Cr+3\oplus$. The curves show that the less hydrated chromium ions in the green salts are reduced and discharged at potentials which are more positive than those at which the more hydrated chromium ions in the violet salts become reduced. This is true of the chloride and sulphate soln., although with the latter the abnormally great displacements of the potentials at which reduction occurs indicate that the complexity of the ions varies with dilution in passing from the green to the violet form. The potentials at which reduction occurs in potassium and rubidium chrome alum soln. are coincident, and indicate the progressive dissociation of the anion complexes. No reduction occurs in alkaline chromium hydroxide soln., which is regarded as proof of the colloidal nature of the hydroxide, in contrast with soln. of zincates and plumbites in which reduction has been observed.

C. Montemartini and L. Losana studied the e.m.f. of soln. of the salt. A. Hagenbach made observations on the thermoelectric force of the soln. E. Feytis found the magnetic susceptibility of the powdered salt to be $11·83\times10^{-6}$ mass units ; J. G. Königsberger found for the soln., 13×10^{-6} mass units at 22° ; and O. Liebknecht and A. P. Wills, 22×10^{-6} mass units at 18°. P. Pascal found the mol. magnetic susceptibility to be $2\times629\times10^{-5}$. L. A. Welo's measurements of the magnetic susceptibility of solid and molten alum are summarized in Fig. 86. The Curie point, $C=\chi(T-\theta)$, for the solid and molten potassium chromic alum are $C_s=2·02$, $C_l=1·67$; $\theta_s=-37°$; and $\theta_l=17°$.

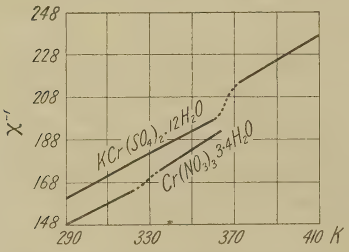


FIG. 86.—The Magnetic Susceptibilities of Hydrated Chromium Salts—Solid and Molten.

N. W. Fischer observed that 100 parts of cold water dissolve 16·7 parts of the chrome alum. J. Locke found that a litre of water dissolves 243·9 grms. of $KCr(SO_4)_2.12H_2O$, or 125·1 grms. of $KCr(SO_4)_2$. The aq. soln. of the violet salt has an acidic reaction, and when the salt has been precipitated many times by alcohol from its aq. soln. H. Baubigny and E. Péchard found that a soln. neutralized by ammonia with methyl-orange as indicator, gave crystals which had an acidic reaction ; and the soln. also reacts acidic after standing a little while. F. P. Venable and F. W. Miller also found that the green modified soln. is also acidic. A. and L. Lumière and A. Seyewetz found that a considerable quantity of alkali-lye can be added to the violet soln. without giving a precipitate ; a soln. of 100 grms. of the alum will take up alkali-lye eq. to 8·435 grms. of H_2SO_4, at ordinary temp. or at 50°, before it yields a permanent turbidity ; at 100°, alkali-lye eq. to 12·8 grms. of H_2SO_4 is similarly taken up. F. Ulffers observed that a cold, conc., aq. soln. of the alum takes up nearly a mol of alkali per gram-atom of chromium, and at the same time the soln. becomes green. According to E. J. Mills and R. L. Barr, a turbidity appears in a soln. of chrome-alum when 2 mols of Na_2CO_3 per mol of $Cr_2(SO_4)_3$ have been added ; and L. Meunier and P. Caste found that chrome alum soln. undergo hydrolysis and the basic chromic salts so formed polymerize under the action of heat and more slowly on keeping. The neutralization of the sulphuric acid formed by the hydrolysis by the sodium carbonate, is accompanied by the liberation of carbon dioxide, and this is expelled from the soln. by increase of temp. or agitation. The precipitation is due to the sodium carbonate acting as a neutralizing agent and also as a coagulating agent on the colloidal soln. of the chromium hydroxide or the polymerized basic chromium salts. For W. J. Chater and J. S. Mudd's observations on the $H^{\cdot}$-ion conc., *vide supra,* chromium sulphate. The electrometric titration curves of H. T. S. Britton for violet and green soln. of chrome-alum are shown in Fig. 79. N. W. Fischer observed that by the spontaneous evaporation, of the violet soln., the salt may be recovered unchanged ; if the soln. be heated between 50° and 75°, it becomes green, and furnishes, on evaporation, a green soluble, amorphous mass or else it yields crystals of potassium sulphate leaving green chromic sulphate in soln. ; but H. Löwel added that the chromic sulphate hinders the crystallization of the potassium sulphate. H. Löwel also observed that if the chrome-alum in a sealed tube be melted in its water of crystallization, and cooled to —20°, there remains a viscid liquid, which, when evaporated at 25° to 30°, loses about 18 mols. of water ; if allowed to stand 2 or 3 weeks under a bell-jar over water, it takes up 15–20 per cent. of the original quantity. If a soln. of alum be dissolved in twice or thrice its weight of water, the green soln. very slowly deposits crystals of chrome-alum. D. Gernez observed that seeding the green liquid with crystals of alum favours the formation of crystals of chrome-alum. V. A. Jacquelain said that the re-formation of crystals of chrome-alum from the green soln. occurs at 2° ; and H. Löwel, at 20° to 30°. H. Löwel also found that if chrome-alum be melted in a sealed tube, or if a soln. of chrome-alum in one or two parts of water be boiled in a flask which is closed while the soln. is boiling, no crystallization occurs even if the vessels be shaken after standing for a year ; but the crystallization of the undercooled or supersaturated liquid starts immediately the vessel is opened.

L. de Boisbaudran observed that the violet soln. prepared in the cold gradually becomes greener ; while the green soln. prepared by heat, slowly becomes blue. In the former case, the soln. increases in vol. owing to the salt giving up combined water ; and in the latter case the soln. decreases in vol. owing to the salt taking up water. K. Grinakowsky said that the absorption spectra, and the electrical conductivities of the soln. indicated that 78° is the transition temp. for the violet to the green soln. The transformation has been discussed by G. D. van Cleeff, M. E. Dougal, W. R. Whitney, A. Recoura, F. P. Venable and F. W. Miller, etc. —*vide supra,* chromic chloride. A. Mitscherlich observed that if the soln.—with or without admixture with potassium sulphate—be heated to 200°, an amorphous precipitate is formed which is supposed to be *chromium-löwigite,* or the *enneahydrate,* $K_2SO_4.Cr_2(SO_4)_3.9H_2O$. F. P. Venable and F. W. Miller said that the same salt is precipitated by adding alcohol to a freshly prepared soln. of the violet salt. According to C. R. C. Tichborne, if a soln. of chrome-alum be heated in sealed tubes for 2 or 3 hrs. at 177°, a basic sulphate is precipitated ; and a dil. soln. of chrome-alum is instantly dissociated, or hydrolyzed when dropped into a flasko of biling water, for the contents of the flask become turbid and opaque. The precipitate redissolves on cooling, and even during boiling if the chrome-alum is gradually added. He concluded that "the green colour of chromic salts is due to the basylous condition"—*vide supra,* H. T. S. Britton's observations. H. Löwel found that barium chloride precipitates all the SO_4 from a cold, freshly prepared, violet soln., but only part of the SO_4 is precipitated from the green soln., so that when the filtrate is heated, the addition of barium chloride precipitates more SO_4. C. Montemartini and L. Losana studied the solubility of the salt in sulphuric acid. According to M. Krüger, alcohol precipitates from the violet soln. the unchanged violet salt—*vide supra*—but the green soln. furnishes a green oily liquid which gradually solidifies, and which contains three-fourths of the SO_4-radicle, the remaining quarter remains dissolved in the alcohol; and M. Siewert added that the oily precipitate contains $K_2O : Cr_2O_3 : SO_3 = 6 : 5 : 18$, and the soln. 2 : 3 : 14. G. N. Wyrouboff observed that the same amount of chromic oxalate is precipitated by the addition of alkali oxalate to the freshly prepared violet soln. as to a soln. which has been kept at 30° for some time. H. Löwel observed that zinc and iron react with a soln. of the salt as in the case of chromic chloride (*q.v.*).

As indicated above, H. Löwel found that if chrome-alum be heated gradually between 300° and 350°, it is transformed into green, anhydrous, $K_2SO_4.Cr_2(SO_4)_3$, which is a pseudomorph after the hydrate, and quickly dissolves in boiling water. If chrome-alum be heated a little above 350°, or, according to C. Hertwig, between 300° and 400°, until all the water is expelled, the anhydrous, green, insoluble salt is formed. This salt, said N. W. Fischer, is lilac-coloured when hot, yellowish-green when cold. C. Hertwig, and H. Löwel found that if the salt be heated just below redness it loses 5·8 per cent. of sulphur trioxide, and at a full red-heat, the chromic sulphate forms chromic oxide. The potassium sulphate can be removed by washing with water. The salt is decomposed if boiled for a long time with alkali-lye with the separation of chromic oxide. The salt is not decomposed by cold or boiling water, hydrochloric acid, sulphuric acid, nitric acid, or aq. ammonia. M. Traube heated potassium dichromate with a large excess of conc. sulphuric acid, and at 160° to 180° obtained a mush of a green, insoluble double salt, and a green liquid; at 240°, there is produced a greyish-red substance. These products contain the more potassium sulphate the lower the temp., and the shorter the time of contact with the acid. W. Wernicke obtained some analogous products.

According to N. W. Fischer, and C. Hertwig, a *dihydrate,* $K_2SO_4.Cr_2(SO_4)_3.2H_2O$, is formed when potassium chrome-alum is heated to 200° so long as it continues to lose water. The dark green, porous residue slowly dissolves when boiled for a long time with water, and more rapidly if hydrochloric acid be present. Water and dil. sulphuric or hydrochloric acid do not act on the salt at ordinary temp. in the course of several days. The salt is decomposed by warm, aq. ammonia which separates as dark-green chromic oxide, soluble in hydrochloric acid. P. N. Pavloff studied the action of soln. of chrome-alum on leather. The *enneahydrate,* $K_2SO_4.Cr_2(SO_4)_3.9H_2O$, and the *tetracosihydrate,* ordinary chrome-alum, have been discussed above. F. Fichter and E. Brunner observed that fluorine is a powerful oxidizing agent. They showed that a soln. of chromium alum, acidified with very dil. sulphuric acid, is not altered by the passage of fluorine for several hours, but if the conc. of free acid is as high as $1{\cdot}5N$, a regular oxidation to chromic acid sets in, and is easily recognized by the change of colour from violet to orange-yellow. Higher conc. of sulphuric acid up to $7{\cdot}5N$ have the same effect. The oxidation is certainly indirect, for if the amount of chromic acid is determined by titration, the fresh soln., which evolves ozone, has about 1·5 times the possible oxidizing power. After standing overnight or heating on a water-bath, the excess of oxidizing substances is destroyed, and the soln. has an oxidizing value corresponding exactly to the theoretical amount of chromic acid. The oxidizing substance must be sulphuric tetroxide, for it is effective at 0°, whereas persulphate oxidizes chromic salts only at higher temp. The conc. sulphuric acid is assumed to exert two functions: (i) to furnish sulphur tetroxide as an intermediate compound; and (ii) to prevent the formation of hydrogen dioxide and hence of perchromic acid which would lead to reduction. According to L. Meunier and P. Caste, the amount of sodium carbonate necessary to produce a permanent precipitate in a soln. of chrome-alum varies with the age and method of preparation of the soln. Immediately after the soln. has been prepared, there is a relatively short period during which the amount of sodium carbonate required increases with the time up to a maximum which varies with the dilution and the temp. This period is longer and more marked the more conc. is the soln. and the lower the temp. After this maximum, there is a relatively long second period, which may last several months during which the amount of sodium carbonate required decreases slowly with the time. At high temp., and particularly at 100°, the two periods are of such short duration that the end of their combined action is almost immediate. It is supposed that immediately on its dissolution in water, chromium sulphate undergoes a partial hydrolysis. The chromium hydroxide and chromium sulphate interact to give a less ionized complex more stable towards sodium carbonate. This process predominates at first. This immediate hydrolysis progresses and is slowly accentuated and the ionic conc. is increased until the second process gradually predominates, with the consequent requirement of less sodium carbonate for the precipitation of the chromium hydroxide. F. E. Brown and J. E. Snyder observed that a crystal of chrome-alum blackens when boiled with vanadium oxytrichloride.

T. Klobb obtained hexagonal crystals of **ammonium potassium chromium sulphate,** $(NH_4,K)_2SO_4.Cr_2(SO_4)_3$, as solid soln. isomorphous with the anhydrous alums, by fusing a mixture of potassium chrome-alum with ammonium sulphate. The salt is not attacked by boiling water. By operating in an analogous manner, **ammonium aluminium chromium sulphate,** $(NH_4)_2SO_4.(Cr,Al)_2(SO_4)_3$, and **ammonium ferric chromium sulphate,** $(NH_4)_2SO_4.(Cr,Fe)_2(SO_4)_3$, were obtained as isomorphous mixtures.

J. H. Gladstone, and H. Erdmann prepared **rubidium chromium sulphate,** or **rubidium disulphatochromiate,** $Rb_2SO_4.Cr_2(SO_4)_3.24H_2O$, or $RbCr(SO_4)_2.12H_2O$, from a soln. of the component salts. It furnishes violet octahedra which, according to O. Pettersson, have the sp. gr. 1·968 at 16·8°. J. H. Gladstone gave 1·946 for the sp. gr. J. Locke said that the salt melts at 107° in its water of crystallization. F. Ephraim and P. Wagner found the vap. press., *p* mm., of the hydrate to be:

	40°	51°	61·5°	71°	79·5°	84°	90°
p . .	25	42	86	166	250	355	414

C. Soret found the index of refraction, μ, for the wave-length, λ at 12° to 17°, to be:

λ .	*G*-line	*F*-line	*b*-line	*E*-line	*D*-line	*C*-line	*B*-line	*A*-line
μ .	1·49323	1·48775	1·48522	1·48486	1·48151	1·47868	1·47756	1·47660

J. H. Gladstone gave for the sp. refraction for the *A*-line $(\mu-1)/D=0·2444$; and for the sp. dispersion $(\mu_A-\mu_G)/D=0·0090$. H. Sauer studied the absorption spectrum. H. Erdmann found that the salt is sparingly soluble in cold water, and that the soln. becomes green when heated. J. Locke gave for the solubility in a litre of water at 25°, 43·4 grms. of the hydrated and 25·7 grms. of the anhydrous salt. N. Demassieux and J. Heyrovsky studied the polarization curves—*vide supra.*

J. H. Gladstone, and C. Soret prepared **cæsium chromium sulphate,** or **cæsium disulphatochromiate,** $Cs_2SO_4.Cr_2(SO_4)_3.24H_2O$, or $CsCr(SO_4)_2.12H_2O$, from a soln. of the component salts. J. H. Gladstone gave 2·043 for the sp. gr. J. Locke found the m.p. to be 116°. F. Ephraim and P. Wagner gave for the vap. press., *p* mm.,

	44°	71·8°	80°	81·5°	90°	95°
p . .	14	119	224	250	411	512

C. Soret observed the index of refraction, μ, for light of wave-length, λ, at 6° to 12°, to be:

λ .	*G*-line	*F*-line	*b*-line	*E*-line	*D*-line	*C*-line	*B*-line	*A*-line
μ .	1·49280	1·48723	1·48491	1·48434	1·48100	1·47836	1·47732	1·47627

J. H. Gladstone gave for the sp. refraction for the A-line $(\mu-1)/D=0\cdot2326$; and for the sp. dispersion, $(\mu_A-\mu_G)/D=0\cdot0086$. H. Sauer studied the absorption spectrum. J. Locke found for the solubility in a litre of water at 25°, 9·4 grms. for the hydrated, and 5·7 grms. for the anhydrous salt. The soln. becomes green above 95°.

E. Carstanjen, J. E. Willm, and O. Pettersson prepared **thallium chromium sulphate,** or **thallium disulphatochromiate,** $Tl_2SO_4.Cr_2(SO_4)_3.24H_2O$, or $TlCr(SO_4)_2.12H_2O$, from a soln. of the component salts. The octahedral crystals appear almost black ; they appear red by transmitted light. J. H. Gladstone gave 2·388 for the sp. gr. ; J. Locke, 92° for the m.p. ; and F. Ephraim and P. Wagner, for the vap. press., p mm.,

	33°	50°	68°	78·5°	87·5°	94°	102°
p . .	8	44	155	250	394	507	672

The index of refraction, μ, for light of wave-length λ at 9° to 25°, was found by C. Soret to be :

λ .	G-line	F-line	b-line	E-line	D-line	C-line	B-line	A-line
μ .	1·53808	1·53082	1·52787	1·52704	1·52280	1·51923	1·51798	1·51692

J. H. Gladstone found the sp. refraction for the A-line to be $(\mu-1)/D=0\cdot2161$; and the sp. dispersion, $(\mu_A-\mu_G)/D=0\cdot0092$. H. Sauer studied the absorption spectrum. J. Locke observed that a litre of water at 25° dissolves 163·8 grms. of the hydrated or 104·8 grms. of the anhydrous salt.

A series of salts of the type $3R_2SO_4.Cr_2(SO_4)_3$, or $R_3Cr(SO_4)_3$, or $R_3[Cr(SO_4)_3]$, has been prepared in the dry way, but not by wet processes. The salts may be identical with A. Recoura's chromotrisulphuric acid. T. Klobb found that when chromic oxide, chloride, or sulphate is fused with ammonium sulphate, **ammonium trisulphatochromiate,** $(NH_4)_3Cr(SO_4)_3$, is formed in pale green, acicular crystals, which become rose-coloured when heated. If the fusion is prolonged, anhydrous ammonium chrome-alum is formed. Ammonium trisulphatochromiate is insoluble in cold water, and it is slightly attacked by boiling water, dil. acids, and dil. alkali-lye. It is not changed at 350°, but it decomposes at a red-heat forming chromic oxide. W. Wernicke prepared **lithium trisulphatochromiate,** $Li_3[Cr(SO_4)_3]$, by fusing chromic oxide with lithium hydrosulphate, adding conc. sulphuric acid to the cold mass, and fusing the mixture again. The properties resembled those of the potassium salt. W. Wernicke obtained **sodium trisulphatochromiate,** $Na_3[Cr(SO_4)_3]$, in a similar manner ; and C. Pagel, by melting a mixture of sodium hydrosulphate, and ammonium and chromic sulphates (5 : 2.5 : 1) as in the case of the potassium salt ; and also by heating sodium dichromate and chloride in the presence of an organic reducing agent, and treating the product with sulphuric acid. The salt forms prismatic or acicular crystals, and behaves like the potassium salt. W. Wernicke obtained **potassium trisulphatochromiate,** $K_3[Cr(SO_4)_3]$, by melting potassium pyrosulphate with anhydrous chrome-alum, or chromic sulphate or oxide, and extracting the cold mass with hot water. A. Étard prepared it by melting chromic chloride and potassium hydrosulphate at a red-heat ; and T. Klobb, by melting a mixture of chrome-alum, and ammonium and potassium sulphates (1 : 4 : 4). The green powder was found by W. Wernicke to appear violet-red when hot ; it consists of six-sided rhombic or hexagonal needles. C. Pagel said that the crystals are hexagonal ; and T. Klobb added that they are probably isomorphous with the corresponding ammonium salt. The compound loses SO_3 when heated to redness, and, according to W. Wernicke, it is insoluble in water, acids, and dil. alkali-lye, but it is decomposed by boiling with conc. potash-lye.

A. Recoura obtained **potassium chromitetrasulphate,** $K_2[Cr_2(SO_4)_4]$, by evaporating on the water-bath a mol of green chromic sulphate with a mol of potassium sulphate ; and the *tetrahydrate,* $K_2[Cr_2(SO_4)_4].4H_2O$, by dehydrating chrome-alum slowly at 110°. The former compound is dark green, and it is soluble in water.

The soln. gives no immediate precipitation with barium chloride, showing that all the SO_4-radicles are masked. The isomeric $(KO)_2Cr_2O_2(SO_3)_4$, or $K_2[Cr(SO_4)_4]$, was obtained from the chromipolysulphuric acid (*q.v.*); and similarly also with **sodium chromitetrasulphate.** A. Recoura obtained **potassium chromipentasulphate,** $K_4[Cr_2(SO_4)_5]$, by evaporating on a water-bath a mol of green chromic sulphate with 2 mols of potassium sulphate; if 3 mols of potassium sulphate are employed, **potassium chromihexasulphate,** $K_6[Cr_2(SO_4)_6]$, is formed. Both these green compounds are soluble in water; and all the SO_4-radicles are masked. G. N. Wyrouboff discussed the composition of these salts—*vide supra*, the corresponding acids.

The mixed crystals of potassium sulphate and chromate were discussed in connection with potassium chromate. A. Recoura obtained **potassium chromitrisulphatochromate,** $K_2[Cr_2(SO_4)_3(CrO_4)]$, by evaporating on a water-bath a soln. of a mol of the green sulphate with a mol of potassium chromate. The dark brown, amorphous product forms a green or brown soln. with water; the aq. soln. readily decomposes into chromic sulphate and potassium chromate. A. Recoura also prepared **potassium chromitrisulphatodichromate,** $K_4[Cr_2(SO_4)_3(CrO_4)_2]$, by using a mol of green chromic sulphate and 2 mols of potassium chromate; with three mols of potassium chromate, **potassium chromitrisulphatotrichromate,** $K_6[Cr_2(SO_4)_3(CrO_4)_3]$, is formed. The properties of these salts are similar. According to A. Étard, a soln. of a mol of potassium chromate and 2 mols of magnesium sulphate furnishes monoclinic prisms of **potassium magnesium disulphatochromate,** $K_2CrO_4.2MgSO_4.9H_2O$, which lose 5 mols. of water at 100°, and all the water at 250°. C. von Hauer said that a third of the SO_4-radicles in $K_2SO_4.MgSO_4.6H_2O$ can be replaced by the CrO_4-radicle without change of form. A. Duffour showed that A. Étard's salt is an arbitrary stage in a series of isomorphous mixtures of $nK_2Cr(SO_4)_2.6H_2O.(1-n)K_2Mg(CrO_4)_2.6H_2O$.

S. M. Jörgensen[2] prepared **chromic hexamminosulphate,** $[Cr(NH_3)_6]_2(SO_4)_3.5H_2O$, by triturating the hexamminobromide with freshly precipitated silver oxide and water; the filtrate was treated with dil. chromic sulphate, and the salt precipitated by alcohol. The yellow needles lose 4 mols. of water over sulphuric acid; and at 100°, the water is expelled in a few hrs. The salt is freely soluble in hot water. It forms a complex chloroplatinate. S. M. Jörgensen, and O. T. Christensen obtained **chromic aquopentamminosulphate,** $[Cr(NH_3)_5(H_2O)]_2(SO_4)_3.3H_2O$, and as in the case of the preceding salt, the prismatic crystals are freely soluble in water; they lose 4 mols. of water between 98° and 100°. The salt forms a complex chloroplatinate. A. Werner and J. L. Klein obtained **chromic tetraquodiamminosulphate,** $[Cr(NH_3)_2(H_2O)_4]_2(SO_4)_3$, by dissolving the bromide in a little dil. hydrobromic acid, adding 8 vols. of absolute alcohol, then adding dil. sulphuric acid, and washing the crystals with alcohol and ether. The reddish-violet plates are very hygroscopic. P. Pfeiffer prepared **chromic tetraquodipyridinosulphate,** $[CrPy_2(H_2O)_4]_2(SO_4)_3.3H_2O$, and also the **hydrosulphate,** $[CrPy_2(H_2O)_4]HSO_4.2H_2O$. For the hexaquo-salts, see the chlorosulphates, and the alums $M[Cr(H_4O_2)_6](SO_4)_2$.

H. J. S. King prepared **chromic hydroxypentamminosulphate,** $[Cr(NH_3)_5(OH)]SO_4$, by the action of a soln. of chloropentamminochloride on ammonium sulphate in conc. aq. ammonia, and precipitation by the addition of alcohol. He gave for the conductivity, μ mhos, of a mol of the salt in v litres:

v . .	32	64	128	256	512	1024	2048
μ 0° .	59·4	69·5	82·0	94·1	108·3	118·9	132·3
25° .	117·6	132·9	158·3	181·2	208·2	234·0	254·2

A. Werner and J. L. Klein, and A. Werner and J. V. Dubsky obtained **chromic hydroxytriaquodiamminosulphate,** $[Cr(NH_3)_2(H_2O)_3(OH)]SO_4.H_2O$, by the action of sulphuric acid on chromic dihydroxydiaquodiamminochlorobromide. The pale red needles were insoluble in water, and soluble in dil. acetic and propionic acids. The acetic acid soln. with potassium thiocyanate forms dihydroxydiaquodiamminothiocyanate. P. Pfeiffer and M. Tapuach, and P. Pfeiffer and W. Osann prepared **chromic hydroxytriaquodipyridinosulphate,** $[CrPy_2(H_2O)_3(OH)]SO_4$. O. T. Christensen obtained **chromic nitritopentamminosulphate,** $[Cr(NH_3)_5(NO_2)]SO_4.H_2O$, by the action of silver sulphate on the chloride of the series. The yellow crystals lose water with decomposition at 100° ; they are freely soluble in water ; and are decomposed by dil. sulphuric acid. S. M. Jörgensen obtained **chromic chloropentamminosulphate,** $[Cr(NH_3)_5Cl]SO_4.2H_2O$, by treating an aq. soln. of the chloride with silver carbonate, and adding dil. sulphuric acid and afterwards alcohol to the filtrate. The carmine-red prisms are freely soluble in water. All the water is expelled in the presence of conc. sulphuric acid, or at 100°, a **hydrosulphate,** $[Cr(NH_3)_5Cl]_4(SO_4)(HSO_4)_6$, was also prepared. A. Benrath found that the chloropentamminosulphate, $[Cr(NH_3)_5Cl]SO_4$, is stable in the presence of 0 to 70 per cent. sulphuric acid, but with more conc. acid, $4[Cr(NH_3)_5Cl]SO_4.3H_2SO_4$ is formed. P. T. Cleve, P. Pfeiffer and S. Basci, P. Pfeiffer and M. Tilgner, and S. M. Jörgensen obtained **chromic chloroaquotetramminosulphate,** $[Cr(NH_3)_4(H_2O)Cl]SO_4$, by the action of cold conc. sulphuric acid on the chloride of the series. The rose-red or dark violet rhombic plates are sparingly soluble in cold water, and freely soluble in warm water. The salt is decomposed by boiling in acidic soln. Y. Shibata measured the absorption spectrum. A. Werner and A. Miolati gave 171·5, 195·1, 226·4, and 262·6 mhos for the conductivity of soln. with a mol of the salt respectively in 250, 500, 1000, and 2000 litres of water at 25°. The pale violet precipitate is hygroscopic. For A. Recoura's, R. F. Weinland and R. Krebs', and R. F. Weinland and T. Schumann's observations on **chromic chloropentaquosulphate,** $[Cr(H_2O)_5Cl]SO_4$, *vide infra.* P. T. Cleve also prepared **chromic bromoaquotetramminosulphate,** $[Cr(NH_3)_4(H_2O)Br]SO_4$, by treating an aq. soln. of the bromide of the series with sodium sulphate and sulphuric acid, and then adding alcohol. The rose-red, crystalline powder is freely soluble in water ; and when the aq. soln. is boiled the salt is decomposed with the deposition of hydrated chromic oxide, and the evolution of ammonia. E. H. Riesenfeld and F. Seemann treated a soln. of chlorodiaquotriamminodichloride with conc. sulphuric acid, and obtained pale violet, hygroscopic crystals of **chromic chlorodiaquotriamminosulphate,** $[Cr(NH_3)_3(H_2O)Cl]SO_4$. S. Guralsky, and A. Werner prepared violet **chromic bromodiaquotriamminosulphate,** $[Cr(NH_3)_3(H_2O)_2Br]SO_4$, by the action of sulphuric acid on the chloride of the series followed by alcoholic precipitation ; and A. Werner and R. Huber, N. Bjerrum and G. H. Hansen prepared **chromic bromopentaquosulphate,** $[Cr(H_2O)_5Br]SO_4.H_2O$, or $CrBrSO_4.6H_2O$.

P. Pfeiffer and M. Tapuach prepared **chromic dihydroxydiaquodipyridinosulphate,** $[CrPy_2(H_2O)_2(OH)_2]_2SO_4.12$ or $14H_2O$; and P. Pfeiffer and P. Koch, **chromic cis-dichlorobisethylenediaminohydrosulphate,** $[Cr\ en_2Cl_2](HSO_4)$. E. Rosenbohm obtained **chromic dichlorotetramminosulphate,** $[Cr(NH_3)_4Cl_2]_2SO_4$, with the magnetic susceptibility $20·68 \times 10^{-6}$ mass units. A. Werner obtained **chromic dichloraquotriamminosulphate,** $[Cr(NH_3)_3(H_2O)Cl_2]_2SO_4$, by treating the chloride of the series with sulphuric acid. The blue needles form a blue soln. with water ; and the salt is reprecipitated by the addition of sulphuric acid. A. Werner, and S. Guralsky prepared dark green crystals of **chromic dibromoaquotriamminosulphate,** $[Cr(NH_3)_3(H_2O)Br_2]_2SO_4$, by the action of sulphuric acid on the bromide of the series. For A. Werner and R. Huber's observations on **chromic dibromotetraquosulphate,** *vide infra.* P. Pfeiffer and P. Koch prepared **chromic cis-dithiocyanatobisethylenediaminohydrosulphate,** $[Cr\ en_2(SCy)_2]HSO_4.1\frac{1}{2}H_2O$; and P. Pfeiffer, the **trans-salt.**

S. M. Jörgensen prepared both the rhodo- and the erythro-salts of **chromic hydroxydecamminosulphate,** $[Cr_2(OH)(NH_3)_{10}]_2(SO_4)_5.2H_2O$, by adding sulphuric acid to an aq. soln. of the thiocyanate of the series. The carmine-red, quadratic or rectangular plates are sparingly soluble in cold water. S. M. Jörgensen prepared carmine-red prismatic crystals of **chromic trihydroxyaquohexamminosulphate,** $[Cr_2(OH)_3(H_2O)(NH_3)_6]_2SO_4.3H_2O$, as well as the **hydrosulphate,** $[Cr_2(OH)(H_2O)(NH_3)_6]HSO_4.\frac{1}{2}H_2O$. P. T. Cleve prepared **chromic decahydroxy-**

tetramminosulphate, $Cr_4(OH)_{10}(SO_4)(NH_3)_4.19H_2O$, by the action of ammonia on ammonium chrome-alum. P. Pfeiffer and W. Vorster prepared **chromic hexahydroxysexiesethylenediaminosulphate,** $[Cr_4(OH)_6en_6](SO_4)_3.10H_2O$. M. Z. Jovitschitsch treated a chromium salt with a little aq. ammonia, and about a gram of the light grey hydroxide treated with just enough sulphuric acid to dissolve it, diluted to about 25 c.c., and mixed with the same vol. of ammonia. A grey precipitate is formed which redissolves in an hour or two. When the soln. is treated with alcohol, the red oil which is formed, when freed from ammonium sulphate, solidifies to a red mass of **chromic dioxyhexamminodisulphate,**

$$\begin{array}{l}(NH_3)_2{=}Cr.O.NH_3.Cr{=}SO_4\\(NH_3)_2{=}\dot{C}r.O.NH_3.\dot{C}r{=}SO_4\end{array}\quad 10H_2O$$

When dried over sulphuric acid, it loses $4H_2O$, but when left in contact with water, it gradually suffers hydrolysis and becomes paler, the acid radicles being partly replaced by hydroxyl groups. It is stable in absolute alcohol, but absorbs carbon dioxide when exposed to the air. D. Strömholm prepared **platinic dihydroxysulphatoctamminochromatodichromate,** $[Pt_2(NH_3)_8(OH)_2SO_4]Cr_2O_7(CrO_4)$, as well as **platinic hydroxysulphatotetramminodichromate,** $[Pt(NH_3)_4(OH)(SO_4)]_2Cr_2O_7$, previously obtained by P. T. Cleve.

H. Schiff prepared the monohydrate of **green chromic chlorosulphate,** $CrClSO_4.H_2O$, by evaporating at about 50° a soln. of basic chromic sulphate in cold hydrochloric acid. A. Recoura, and A. Werner and R. Huber obtained the *hexahydrate* by boiling for a quarter of an hour 60 grms. of violet chromic sulphate with 50 c.c. of fuming hydrochloric acid, and allowing the mixture to stand for some days. R. F. Weinland and R. Krebs obtained the *octohydrate* by evaporating at 10° over conc. sulphuric acid a mixture of a conc. aq. soln. of the green chloride with an eq. quantity of sulphuric acid; and R. F. Weinland and T. Schumann, and N. Bjerrum also obtained it from one of the chromic chlorides and sulphuric acid. H. Schiff described his monohydrate as a green, hygroscopic, amorphous mass; A. Werner and R. Huber described his hexahydrate as a bluish-green mass of tabular crystals; and R. F. Weinland and co-workers found the octohydrate forms pale green masses of tabular crystals. A. Recoura, and R. F. Weinland and co-workers said that a *pentahydrate* is formed by heating the higher hydrate at 85°, or exposing it in vacuo over sulphuric acid. A soln. of the salt gives no immediate precipitation with silver nitrate, but a precipitate with barium chloride is formed at once showing that the chloride radicle is masked, but not so with the sulphate radicle. The lowering of the f.p. is rather greater than would correspond with that for the non-oxidized molecule; and the mol. conductivity 76·5 for $v=125$ at 1° corresponds with the dissociation of the salt into two ions. The conductivity gradually increases when the soln. is allowed to stand showing that the salt is gradually resolved into three ions as it is transformed into the violet salt. The formula for **chromic chloropentaquosulphate,** $[Cr(H_2O)_5Cl]SO_4nH_2O$, fits the facts very well; and this, changing to the violet salt, forms $[Cr(H_2O)_6](SO_4)Cl.nH_2O$. N. Bjerrum discussed the case where the sulphate radicle is not immediately precipitable. L. A. Welo gave $19{\cdot}86\times10^{-6}$ for the magnetic susceptibility of $[Cr(H_2O)_6]ClSO_4.2H_2O$, and $19{\cdot}62\times10^{-6}$ for $[Cr(H_2O)_5Cl]SO_4.3H_2O$.

R. F. Weinland and R. Krebs obtained the *octohydrate* of **violet chromic chlorosulphate,** $CrClSO_4.8H_2O$, by mixing 26·6 grms. of the greyish-blue $CrCl_3.6H_2O$ dissolved in 28 grms. of water, with 10 grms. of conc. sulphuric acid mixed with 18 grms. of water, all well cooled. Violet acicular crystals of the salt separate in a few days as the mixture is evaporated in a desiccator; if 11 grms. of water and 10 grms. of conc. sulphuric acid are used tabular crystals are formed. If the octohydrate is kept over sulphuric acid in vacuo it forms the *hexahydrate*. An aq. soln. of the salt evaporated over sulphuric acid yields violet chromic sulphate. An acidified soln., at 0°, gives an immediate precipitation of silver chloride when treated with silver nitrate, but barium sulphate is not at once precipitated by barium chloride. The mol. conductivity is 116 for $v=125$ at 1°, showing that the salt is not all ionized into three ions. The lowering of the f.p. also gives values rather larger than those required for the non-ionized molecule. The facts are considered to fit the formula for **chromic hexaquochlorosulphate,** $[Cr(H_2O)_6](SO_4)Cl.nH_2O$. A. del Campo and co-workers obtained the violet salt by the action of hydrogen chloride on a cold, conc. soln. of the violet chromic sulphate. E. Moles and M. Crespi gave 1·799 for the sp. gr. of $[Cr(H_2O)_6]Cl(SO_4).H_2O$, at 25°/4°, and 171 for the mol. vol. According to A. Werner and R. Huber, by mixing conc. soln. of violet chromic sulphate, and green chromic chloride, and adding conc. sulphuric acid while the mixture is cooled with iced water, green crystals of the bimolecular, green chlorosulphate, $(CrClSO_4.6H_2O)_2$, thought by A. Werner and R. Huber, and N. Bjerrum to be **chromic dichlorotetraquochromihexaquodisulphate,** $[Cr(H_2O)_6](SO_4)_2[Cr(H_2O)_4Cl_2].2H_2O$. The aq. soln. does not give an immediate precipitation with silver nitrate, but, it does give one with barium chloride. A 1 : 10-soln. of the salt in dil. hydrochloric acid, when sat. with hydrogen chloride, precipitates half the chromium as blue chromic chloride. N. Bjerrum and G. H. Hansen likewise prepared **chromic dichlorotetraqualuminohexaquodisulphate,** $[Cr(H_2O)_4Cl_2][Al(H_2O)_6(SO_4)_2.2H_2O$; and **chromic dichlorotetraquovanadihexaquodisulphate,** $[Cr(H_2O)_4Cl_2][V(H_2O)_6](SO_4)_2.2H_2O$, by the electrolytic reduction of vanadyl sulphate in the presence of chromic chloride. A. Werner and R. Huber, and N. Bjerrum and G. H. Hansen obtained **chromic dibromotetraquochromihexaquodisulphate,** $[Cr(H_2O)_6](SO_4)_2[Cr(H_2O)_4Br_2].2H_2O$, by the action of hydrogen bromide as in the analogous case of the preceding salt. The dark green plates are soluble in water; and are precipitated from the aq. soln. by sulphuric acid. N. Bjerrum and G. H. Hansen likewise prepared **chromic dibromotetraquoaluminohexaquodisulphate,** $[Cr(H_2O)_4Br_2][Al(H_2O)_6](SO_4)_2.2H_2O$, as well as the corresponding **chromic dibromotetraquoferrihexaquodisulphate,** $[Cr(H_2O)_4Br_2][Fe(H_2O)_6](SO_4)_2.2H_2O$; and dark green crystals of **chromic dibromotetraquovanadihexaquodisulphate,** $[Cr(H_2O)_4Br_2][V(H_2O)_6](SO_4)_2.2H_2O$, by the electrolysis of vanadyl sulphate in the presence of chromic bromide. The corresponding titanium and manganese salts could not be prepared.

S. M. Jörgensen prepared yellow octahedral crystals of **chromic hexamminoiodosulphate,** $[Cr(NH_3)_6](SO_4)I$, by adding ammonium iodide and sulphate to an ammoniacal soln. of the chloride of the series.

N. Larsson prepared **ammonium chromic chloropentaquodichlorosulphate,** $[CrCl(H_2O)_5]Cl_2.(NH_4)_2SO_4.H_2O$, by adding ammonium sulphate to a well-cooled soln. of chromic chloropentaquodichloride; **ammonium chromic chloropentaquodisulphate,** $[CrCl(H_2O)_5]SO_4.(NH_4)_2SO_4$, by adding alcohol to a cold soln. after boiling a mixture of soln. of chromic chloropentaquodichloride and ammonium sulphate; if the soln. contains sulphuric acid, **ammonium chromic chloropentaquosulphatohydrosulphate,** $[CrCl(H_2O)_5]SO_4(NH_4)HSO_4$, is formed; likewise with **hydroxylamine chromic chloropentaquochlorosulphate,** $[CrCl(H_2O)_5]Cl(SO_4).(NH_4O)_2SO_4.2H_2O$; and **hydroxylamine chromic chloropentaquosulphatohydrosulphate,** $[CrCl(H_2O)_5]SO_4.(NH_4O)HSO_4$. Complexes were also prepared with sulphates of *organic* bases—methylammonium, dimethylammonium, tetramethylammonium, ethylammonium, pyridinium, and strychnine.

R. F. Weinland and T. Schumann observed that a soln. of green hydrated chromic chloride and ammonium sulphate in equimolar proportions deposits crystals of **ammonium chromic trichlorodisulphate,** $CrCl_3.2(NH_4)_2SO_4.6H_2O$, or **ammonium chromic trichlorotetraquodisulphate,** $[Cr(H_2O)_4Cl_2]Cl.2(NH_4)_2SO_4.2H_2O$, in the form of large, green, four- or six-sided plates when kept a short time in a desiccator. Only one-third of the chlorine is precipitated immediately by silver nitrate from an acidified soln. of the salt at 0°, whereas all the sulphate is thrown down immediately by barium chloride. N. Larsson prepared this salt as well as **ammonium chromic dichlorotetraquochlorotrisulphate,** $[CrCl_2(H_2O)_4]Cl.3(NH_4)_2SO_4.2H_2O$; and

N. Larsson, and R. F. Weinland and T. Schumann found that **ammonium chromic dichlorohydrosulphatotrisulphate,** $[Cr(H_2O)_4Cl_2]_2SO_4.2(NH_4)_3SO_4(HSO_4)$, separates in green needles from a soln. containing a mol of green hydrated chromic chloride, a mol of ammonium sulphate, and 1 to 3 mols of sulphuric acid. In an acidified soln. of the salt at 0°, silver nitrate does not produce an immediate precipitate, but all the sulphate is at once thrown down by barium chloride. N. Larsson found that chromium dichlorotetraquosulphate forms complex salts with the sulphates of organic bases—methylammonium, tetramethylammonium, ethylammonium, tetraethylammonium, guanidinium, and pyridinium.

J. Meyer and V. Stateczny[3] obtained indications of the existence of **chromyl sulphuryl chloride,** $CrSO_5Cl_2$, formed by the action of sulphur trioxide on a well-cooled soln. of chromyl chloride in carbon tetrachloride, and the mixture heated in a sealed tube at 120°. The brown product fumes in air, it is decomposed by water into sulphur trioxide and chromyl chloride.

REFERENCES.

[1] A. Mussin-Puschkin, *Crell's Ann.*, i, 355, 1798 ; ii, 444, 1798 ; i, 187, 1800 ; ii, 267, 1801 ; A. Schrötter, *Pogg. Ann.*, **53**. 528, 1841 ; J. J. Berzelius, *ib.*, **1**. 34, 1824 ; *Schweigger's Journ.*, **22**. 53, 1818 ; N. W. Fischer, *Kastner's Arch.*, **14**. 164, 1828 ; **16**. 212, 1829 ; M. Traube, *Liebig's Ann.*, **66**. 169, 1848 ; O. Schumann, *ib.*, **187**. 307, 1877 ; H. Schiff, *ib.*, **107**. 81, 1858 ; **124**. 174, 1862 ; M. Siewert, *ib.*, **126**. 88, 1863 ; E. S. Hedges and J. E. Myers, *Journ. Chem. Soc.*, **127**. 2432, 1925 ; H. Löwel, *Journ. Pharm. Chim.*, (3), **4**. 321, 1845 ; *Ann. Chim. Phys.*, (3), **44**. 320, 1855 ; J. E. Willm, *Ann. Chim. Phys.*, (4), **5**. 5, 1865 ; E. A. Werner, *Chem. News*, **56**. 277, 1887 ; D. M. Torrance and N. Knight, *ib.*, **117**. 270, 1918 ; H. M. Vernon, *ib.*, **66**. 104, 114, 141, 152, 1892 ; H. N. Warren, *ib.*, **60**. 237, 1889 ; C. R. C. Tichborne, *ib.*, **24**. 199, 209, 1871 ; *Bull. Soc. Chim.*, (2), **17**. 25, 1872 ; *Proc. Irish Acad.*, **1**. 169, 1874 ; A. Polis, *Ber.*, **13**. 360, 1880 ; F. Rüdorff, *ib.*, **21**. 3044, 1882, 1888 ; I. Koppel, *ib.*, **39**. 3738, 1906 ; W. Meyeringh, *ib.*, **10**. 1946, 1877 ; W. Müller-Erzbach, *ib.*, **21**. 2223, 1888 ; *Zeit. phys. Chem.*, **2**. 545, 1888 ; J. W. Retgers, *ib.*, **16**. 624, 1895 ; E. Moles and M. Crespi, *ib.*, **130**. 337, 1927 ; R. Hollmann, *ib.*, **37**. 193, 1901 ; G. Städeler, *Journ. prakt. Chem.*, (1), **76**. 54, 1859 ; R. Böttger, *ib.*, (1), **36**. 318, 1845 ; E. Carstanjen, *ib.*, (1), **102**. 65, 1867 ; B. Franz, *ib.*, (2), **5**. 289, 1872 ; G. D. van Cleeff, *ib.*, (2), **23**. 72, 1881 ; F. Ulffers, *ib.*, (2), **76**. 161, 1907 ; A. Mitscherlich, *ib.*, (1), **83**. 477, 1861 ; C. Pape, *Pogg. Ann.*, **125**. 513, 1865 ; C. Hertwig, *ib.*, **56**. 95, 1842 ; *Liebig's Ann.*, **54**. 271, 1842 ; **55**. 298, 1843 ; W. Wernicke, *Pogg. Ann.*, **159**. 575, 1876 ; M. Krüger, *ib.*, **61**. 218, 1844 ; C. F. Rammelsberg, *ib.*, **91**. 351, 1854 ; J. L. Howe and E. A. O'Neal, *Journ. Amer. Chem. Soc.*, **20**. 763, 1898 ; F. E. Brown and J. E. Snyder, *ib.*, **47**. 2671, 1925 ; F. P. Venable and F. W. Miller, *ib.*, **20**. 484, 1898 ; W. R. Whitney, *ib.*, **21**. 1075, 1899 ; *Zeit. phys. Chem.*, **20**. 40, 1896 ; C. Soret, A. Borel and E. Dumont, *Arch. Sciences Genève*, (4), **3**. 376, 1897 ; C. Soret, *ib.*, (3), **13**. 16, 1885 ; (3), **20**. 520, 1888 ; *Compt. Rend.*, **99**. 868, 1884 ; **101**. 156, 1885 ; P. A. Favre and C. A. Valson, *ib.*, **74**. 1016, 1165, 1872 ; **75**. 798, 925, 1000, 1872 ; F. Jean, *ib.*, **68**. 198, 1869 ; A. Recoura, *ib.*, **114**. 479, 1892 ; **116**. 1367, 1893 ; **111**. 934, 1897 ; *Ann. Chim. Phys.*, (7), **4**. 515, 1895 ; *Bull. Soc. Chim.*, (3), **9**. 590, 1893 ; (3), **9**. 586, 1893 ; (3), **17**. 934, 1897 ; P. de Boissieu, *ib.*, (2), **47**. 494, 1887 ; H. Lescœur and D. Mathurin, *ib.*, (2), **50**. 39, 1888 ; A. and L. Lumière and A. Seyewetz, *ib.*, (3), **27**. 1073, 1902 ; G. N. Wyrouboff, *ib.*, (2), **27**. 676, 1902 ; T. Klobb, *ib.*, (3), **9**. 666, 1893 ; *Compt. Rend.*, **117**. 312, 1893 ; C. Pagel, *ib.*, **130**. 1030, 1900 ; A. Étard, *ib.*, **84**. 1089, 1877 ; **85**. 444, 1877 ; **86**. 1399, 1878 ; **120**. 1057, 1895 ; P. Pascal, *ib.*, **147**. 742, 1908 ; E. Feytis, *ib.*, **156**. 886, 1913 ; L. Meunier and P. Caste, *ib.*, **172**. 1488, 1921 ; E. J. Maumené, *ib.*, **103**. 1140, 1886 ; *Bull. Soc. Chim.*, (2), **46**. 261, 1886 ; F. Ephraim, *Ber.*, **50**. 1069, 1088, 1917 ; F. Ephraim and P. Wagner, *ib.*, **50**. 1088, 1917 ; G. Beck, *ib.*, **174**. 31, 1928 ; L. Vegard and H. Schjelderup, *Ann. Physik*, (4), **54**. 146, 1918 ; L. Vegard, *ib.*, (4), **63**. 753, 1920 ; L. Vegard and E. Esp, *ib.*, (4), **85**. 1152, 1928 ; L. Vegard and A. Maurstad, *Zeit. Kryst.*, **69**. 519, 1929 ; C. Schaefer and M. Schubert, *Ann. Physik*, (4), **50**. 283, 1916 ; (4), **59**. 583, 1919 ; O. Liebknecht and A. P. Wills, *ib.*, (4), **1**. 178, 1900 ; H. du Bois and G. J. Elias, *ib.*, (4), **27**. 233, 1908 ; J. G. Königsberger, *ib.*, (4), **6**. 506, 1901 ; *Wied. Ann.*, **66**. 698, 1898 ; K. Grinakowsky, *Journ. Russ. Phys. Chem. Soc.*, **44**. 802, 1912 ; C. Montemartini and L. Losana, *Notiz. Chim. Ind.*, **2**. 551, 1927 ; H. Jaffe, *Ueber die Absorptionsverhältnisse einiger Chrom- und Eisensalzlösungen im kurzwelligen Spektralgebiete*, Potsdam, 1909 ; A. Byk and H. Jaffe, *Zeit. phys. Chem.*, **68**. 323, 1909 ; A. Eucken and G. Kuhn, *ib.*, **134**. 193, 1928 ; E. I. Orloff, *Ukrain. Chem. Journ.*, **3**. 115, 1928 ; A. Beutel, *Oesterr. Chem. Ztg.*, **19**. 123, 1916 ; J. Thomsen, *Thermochemische Untersuchungen*, Leipzig, **3**. 190, 1882 ; A. Duffour, *Bull. Soc. Min.*, **42**. 247, 1919 ; S. Higuchi, *Science Rep. Tohoku Univ.*, **12**. 359, 1924 ; P. Hasenclever, *U.S. Pat. No.* 1486961, 1924 ; A. Fock, *Zeit. Kryst.*, **28**. 388, 1897 ; G. Tammann and A. Sworykin, *Zeit. anorg. Chem.*, **173**. 73, 1928 ; A. Benrath, *ib.*, **177**. 286, 1928 ; W. J. Chater and J. S. Mudd, *Journ. Soc. Leather Trades' Chem.*, **12**. 272, 1928 ; G. Canneri, *Gazz. Chim. Ital.*, **55**. 611, 1925 ; W. Haidinger, *Edin. Journ. Science*, **1**. 99, 1924 ; F. Klocke, *Zeit. Kryst.*,

2. 126, 1878 ; J. Beckenkamp, *ib.*, **12**. 419, 1887 ; E. S. von Fedoroff, *ib.*, **52**. 626, 1913 ; P. N. Pawloff, *ib.*, **42**. 120, 1906 ; J. H. Gladstone, *Phil. Mag.*, (5), **20**. 162, 1885 ; R. F. d'Arcy, *ib.*, (5), **28**. 230, 1889 ; W. Spring, *Bull. Acad. Belg.*, (3), **3**. 331, 1882 ; *Ber.*, **15**. 1254, 1882 ; **17**. 410, 1884 ; H. Kopp, *Liebig's Ann. Suppl.*, **3**. 333, 1865 ; L. Meunier, *Journ. Soc. Leather Trades Chem.*, **5**. 103, 1921 ; A. Lielegg, *Dingler's Journ.*, **207**. 321, 1873 ; A. Stiassny, *ib.*, **202**. 191, 1871 ; *Journ. Chem. Soc.*, **25**. 188, 1872 ; N. Demassieux and J. Heyrovsky, *Journ. Chim. Phys.*, **26**. 219, 1929 ; L. A. Welo, *Nature*, **124**. 575, 1929 ; W. N. Hartley, *Trans. Roy. Dublin. Soc.*, (2), **7**. 253, **1900** ; *Chem. News*, **65**. 15, 1892 ; *Proc. Roy. Soc.*, **21**. 499, 1873 ; G. D. Liveing and J. Dewar, *ib.*, **35**. 73, 1883 ; J. Dewar, *Chem. News*, **85**. 277, 1902 ; F. Krauss, A. Fricke and H. Querengässer, *Zeit. anorg. Chem.*, **181**. 38, 1929 ; L. Playfair and J. P. Joule, *Mem. Chem. Soc.*, **2**. 401, 1845 ; *Journ. Chem. Soc.*, **1**. 121, 1849 ; W. A. Tilden, *ib.*, **45**. 267, 1884 ; E. J. Mills and R. L. Barr, *ib.*, **41**. 341, 1882 ; F. Fichter and E. Brunner, *ib.*, 1862, 1928 ; M. E. Dougall, *ib.*, **69**. 1526, 1896 ; *Chem. News*, **74**. 278, 1896 ; G. T. Gerlach, *Zeit. anal. Chem.*, **28**. 497, 1889 ; H. C. Jones and W. W. Strong, *Phys. Zeit.*, **10**. 499, 1909 ; H. C. Jones and E. Mackay, *Zeit. Elektrochem.*, **4**. 235, 1898 ; *Amer. Chem. Journ.*, **19**. 107, 1897 ; S. F. Howard and H. C. Jones, *ib.*, **48**. 500, 1913 ; H. H. Hosford and H. C. Jones, *ib.*, **46**. 240, 1911 ; J. Locke, *ib.*, **26**. 166, 1901 ; M. Bamberger and R. Grengg, *Centr. Min.*, 65, 1921 ; H. Baubigny and E. Péchard, *Compt. Rend.*, **115**. 604, 1892 ; D. Gernez, *ib.*, **79**. 1332, 1874 ; V. A. Jacquelain, *ib.*, **24**. 439, 1847 ; L. de Boisbaudran, *ib.*, **79**. 1491, 1874 ; *Bull. Soc. Min.*, **2**. 39, 1879 ; M. C. Lea, *Zeit. anorg. Chem.*, **4**. 445, 1893 ; *Amer. Journ. Science*, (3), **45**. 478, 1893 ; C. von Hauer, *Sitzber. Akad. Wien*, **39**. 441, 1860 ; **53**. 221, 1866 ; A. Hagenbach, *Wied. Ann.*, **53**. 466, 1894 ; O. Knoblauch, *ib.*, **43**. 738, 1891 ; F. S. Svenson, *Ueber die electrische Leitungsfähigkeit bei einigen Electrolyten*, Lund, 1878 ; J. Juttke, *Ueber die Bindung des Krystallwassers in einiger Alaunen*, Berlin, 1887 ; J. H. Kastle, *Amer. Chem. Journ.*, **23**. 500, 1900 ; F. Oltmanns, *Pharm. Centrh.*, **51**. 200, 1910 ; Y. Shibata, *Journ. Coll. Science Tokyo*, **41**. 6, 1919 ; C. Doelter, *Monatsh.*, **29**. 1145, 1908 ; H. T. S. Britton, *Ind. Chemist*, **3**. 452, 1927 ; *Journ. Chem. Soc.*, **127**. 2120, 1925 ; *ib.*, **129**. 269, 1926 ; F. Schmidt, *Beiträge zur elektrolytischen Oxydation des Chroms*, Berlin, 54, 1909 ; H. C. Starck, *German Pat., D.R.P.* 419365, 1923 ; E. Dittler, *Zeit. anorg. Chem.*, **168**. 309, 1928 ; H. Erdmann, *Arch. Pharm.*, **232**. 3, 1894 ; F. L. S. Jones, *Journ. Ind. Eng. Chem.*, **15**. 265, 1923 ; O. Pettersson, *Acta Soc. Upsala*, (3), **9**. 4, 1879 ; *Ber.*, **9**. 1559, 1676, 1876 ; P. N. Pavloff, *Koll. Zeit.*, **36**. 217, 1925 ; H. W. Vogel, *Praktische Spectralanalyse iridischer Stoffe*, Berlin, 1889 ; *Sitzber. Akad. Berlin*, 412, 1878 ; *Ber.*, **11**. 913, 1368, 1562, 1878 ; K. Vierordt, *ib.*, **5**. 34, 1872 ; M. A. Rakuzin and A. Rosenfeld, *Chem. Ztg.*, **51**. 638, 1927 ; M. A. Rakuzin and M. Gönke, *Mitt. Wiss. Tech. Russ.*, 15, 1924 ; A. N. Bach, 163, 1923 ; P. T. Cleve, *Svenska Akad. Handl.*, **6**. 4, 1865 ; A. Ferrero, *Nuovo Cimento*, (5), **1**. 285, 1901 ; V. Monti, *ib.*, (4), **43**. 212, 1896 ; *Atti Accad. Torino*, **30**. 704, 1895 ; *Zeit. anorg. Chem.*, **12**. 75, 1896 ; F. Sommer and K. Weise, *ib.*, **94**. 70, 1916 ; W. Böhlendorff, *Studien zur Absorptionsspectralanalyse*, Erlangen, 1890 ; J. M. Hiebendaal, *Onderzoek over eenige absorptiespectra*, Utrecht, 1873 ; J. Formanek, *Die qualitative Spectralanalyse anorganischer und organischer Körper*, Berlin, 1905 ; H. Sauer, *Die linienhafte Absorption der Chromalaunkristalle*, Leipzig, 1928 ; *Ann. Physik*, (4), **87**. 197, 1928 ; F. A. Rohrman and N. W. Taylor, *Journ. Chem. Education*, **6**. 473, 1929 ; J. M. Cork, *Phys. Rev.*, (2), **31**. 160, 1928 ; J. Hertkorn, *German Pat., D.R.P.* 265046, 1913 ; H. Chaumat, *French Pat. No.* 450677, 1912 ; *Brit. Pat. No.* 1636, 1913 ; T. Ishikawa, *Bull. Japan. Chem. Soc.*, **1**. 139, 1926 ; P. W. Bridgman, *Proc. Amer. Acad.*, **64**. 51, 1929 ; F. A. Rohrman and N. W. Taylor, *Journ. Chem. Education*, **6**. 473, 1929 ; A. W. Gregory, *Brit. Pat. No.* 17672, 1912 ; O. Nydegger, *ib.*, 198645, 1923 ; T. V. Barker, *Min. Mag.*, **15**. 42, 1908.

[2] H. Schiff, *Liebig's Ann.*, **124**. 176, 1862 ; H. J. S. King, *Journ. Chem. Soc.*, **125**. 1329, 1924 ; **127**. 2100, 1925 ; A. Recoura, *Bull. Soc. Chim.*, (3), **27**. 1155, 1902 ; *Compt. Rend.*, **135**. 163, 1902 ; A. del Campo, F. Manzano and A. Mallo, *Anal. Fis. Quim.*, **25**. 186, 1927 ; A. Werner and A. Miolati, *Zeit. phys. Chem.*, **14**. 516, 1894 ; A. Werner, *Ber.*, **39**. 3665, 1906 ; **43**. 2286, 1910 ; A. Werner and J. V. Dubsky, *Ber.*, **40**. 4092, 1907 ; J. V. Dubsky, *Ueber basische Salze, deren Zusammensetzung und Beziehungen*, Zürich, 1908 ; A. Werner and R. Huber, *Ber.*, **39**. 330, 1906 ; A. Werner and J. L. Klein, *ib.*, **35**. 288, 1902 ; J. L. Klein, *Ueber Tetraquodiammin- und Diacidodiaquodiammin-Chromsalze*, Zürich, 1902 ; N. Bjerrum, *Zeit. phys. Chem.*, **59**. 598, 1907 ; N. Bjerrum and G. H. Hansen, *Zeit. anorg. Chem.*, **63**. 157, 1909 ; *Ber.*, **39**. 1597, 1906 ; **40**. 2918, 3948, 1907 ; R. F. Weinland and T. Schumann, *ib.*, **40**. 3091, 3768, 1907 ; T. Schumann, *Ueber Chromiaquoverbindungen*, Tübingen, 1908 ; R. F. Weinland and R. Krebs, *Zeit. anorg. Chem.*, **48**. 252, 1906 ; **49**. 160, 1906 ; R. Krebs, *Ueber Chromchloridsulfate und Chromsulfate*, Tübingen, 1906 ; E. H. Riesenfeld and F. Seemann, *Ber.*, **42**. 4222, 1909 ; F. Seemann, *Ueber Chromi-aquo-Triammine*, Freiburg, 1910 ; S. M. Jörgensen, *Journ. prakt. Chem.*, (2), **20**. 121, 1879 ; (2), **25**. 339, 1882 ; (2), **30**. 24, 1884 ; (2), **31**. 80, 1885 ; (2), **42**. 208, 1890 ; (2), **45**. 269, 1892 ; O. T. Christensen, *ib.*, (2), **39**. 1881, (2), **24**. 83, 1881 ; E. Rosenbohm, *Zeit. phys. Chem.*, **93**. 693, 1919 ; E. Moles and M. Crespi, *ib.*, **130**. 337, 1927 ; P. Pfeiffer, *Zeit. anorg. Chem.*, **29**. 122, 1901 ; **31**. 433, 1902 ; M. Tapuach, *Zur Kenntnis der Hydratisomerie bei Di- und Trihalogenochromsalzen*, Zürich, 1907 ; P. Pfeiffer and M. Tapuach, *Ber.*, **39**. 1874, 1906 ; W. Osann, *Zur Chemie der Dipyridinchromsalze*, Zürich, 1907 ; P. Pfeiffer and W. Osann, *ib.*, **40**. 4032, 1907 ; P. Pfeiffer and S. Basci, *Ber.*, **38**. 3595, 1905 ; S. Basci, *Beitrag zur Chemie ammoniakalischer Chromsalze*, Zürich, 1907 ; P. Pfeiffer and P. Koch, *ib.*, **37**. 4282, 1904 ; P. Koch, *Beitrag zur Stereoisomerie der Chromsalze*, Zürich, 1905 ; P. Pfeiffer and M. Tilgner, *Zeit. anorg. Chem.*, **55**. 370, 1907 ; P. Pfeiffer and W. Vorster, *ib.*, **58**. 286, 1908 ; D. Strömholm, *ib.*, **108**. 184, 1919 ; N. Larsson, *ib.*, **110**. 153,

1920; P. T. Cleve, *Oefvers. Akad. Förh.*, 172, 1861; *Svenska Akad. Handl.*, **6**. 4, 1865; *Acta Soc. Upsala*, (3), **6**. 81, 1868; L. A. Welo, *Phil. Mag.*, (7), **6**. 481, 1928; S. Guralsky, *Ueber Di- und Triamminchromisalze*, Zürich, 1909; M. Z. Jovitschitsch, *Monatsh.*, **34**. 225, 1913; *Helvetica Chim. Acta*, **3**. 46, 1920; *Compt. Rend.*, **158**. 872, 1914; A. Benrath, *Zeit. anorg. Chem.*, **177**. 286, 1928; Y. Shibata, *Journ. Coll. Science Tokyo*, **41**. 6, 1919.

[3] V. Stateczny, *Ueber einige Heteropolysäuren von Elementen der Schwefelgruppe*, Breslau, 1922; J. Meyer and V. Stateczny, *Zeit. anorg. Chem.*, **122**. 1, 1922.

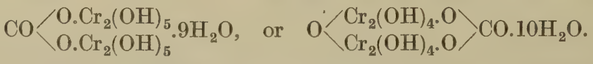
§ 31. Chromium Carbonates

According to A. Moberg,[1] the precipitate produced by adding an alkali carbonate to a soln. of chromous chloride is supposed to be **chromous carbonate,** $CrCO_3$, which is similar in many respects to magnesium, zinc, and ferrous carbonates. When chromous chloride is added to a boiling soln. of potassium carbonate, the reddish-brown precipitate gradually acquires a bluish-green colour provided air be excluded, and the supernatant liquor becomes yellow, and deposits brown-yellow plates, which, when exposed to air, become opaque and green. If these be now placed in water, a yellow soln. and a greenish-blue residue are formed. Again, if a cold soln. of potassium carbonate, freed from air, is employed, a dense yellow powder may be precipitated, or bluish-green flakes—of the same composition—may appear. If the yellow or brownish-red liquid be exposed to air, it turns green, and deposits a green substance; if the liquid be kept in closed vessels, carbon dioxide is evolved and the liquid becomes turbid, and deposits a green, flocculent precipitate which also gives off carbon dioxide, and hydrogen, forming brown, hydrated chromosic oxide. The precipitate obtained with the cold soln. of potassium carbonate, on boiling, gives off carbon dioxide, and then dissolves in acids without effervescence. If potassium hydrocarbonate be employed, a similar product is obtained but containing more carbon dioxide, while the liquid retains more chromous carbonate in soln. H. Moissan obtained the carbonate of a high degree of purity, by adding sodium carbonate to a soln. of chromous chloride while air is excluded. The amorphous, greyish-white carbonate takes up oxygen from air, and when heated it forms chromic oxide and carbon monoxide; it is sparingly soluble in water sat. with carbon dioxide; if allowed to stand in water exposed to air, it becomes red and then changes to bluish hydrated chromic oxide.

G. Baugé prepared a series of double carbonates by the action of a carbonate on moist chromous acetate or tartrate in an atm. of carbon dioxide. He obtained **ammonium chromous carbonate,** $(NH_4)_2CO_3.CrCO_3.H_2O$, by passing a current of carbon dioxide through an ammoniacal soln. of chromous acetate, and washing the precipitate successively with aq. ammonia, alcohol, and ether, and dried in a current of hydrogen charged with ammonia. The same salt was obtained by boiling a soln. of chromous acetate in ammonia with sodium carbonate in a current of hydrogen. The yellow, crystalline powder, when thoroughly dried, is fairly stable in dry air. It is very active chemically. In air, it forms chromic hydroxide, with chlorine it forms chromic chloride; it dissolves in hydrochloric or sulphuric acid forming a blue soln. if air be absent; and hydrogen sulphide converts it into chromic sulphide. G. Baugé obtained impure **lithium chromous carbonate** by adding lithium carbonate to chromous acetate suspended in water. According to G. Baugé, when well washed and moist chromous acetate is mixed with a soln. of sodium carbonate, it first dissolves, and after a time a reddish-brown compound separates; this is washed with water, and afterwards with 98 per cent. alcohol, all the operations being conducted in an atm. of carbon dioxide. When dried in a current of the same gas, the resulting *decahydrate* of **sodium chromous carbonate,** $Na_2CO_3.CrCO_3.10H_2O$, forms microscopic, tabular lozenge-shaped crystals which lose water in vacuo at the ordinary temp. or at 100°. It is very soluble in cold water, but the solubility gradually diminishes, probably in consequence of polymerization. It is a powerful reducing agent, and decomposes water at a little below

100° with liberation of hydrogen. When exposed to dry air, it effloresces, and is afterwards converted into a mixture of sodium carbonate and chromic hydroxide; in moist air, it oxidizes rapidly with development of heat. Chlorine converts it into chromic oxide with liberation of carbon dioxide; hydrogen and hydrogen sulphide have no action on it in the cold, and when heated at 100° in a current of these gases, it yields the monohydrate. Dil. hydrochloric and sulphuric acids dissolve the salt, forming blue soln. The *monohydrate*, $Na_2Cr(CO_3)_2.H_2O$, obtained by the action of a current of an inert gas at 100°, is a yellow powder which becomes brown when heated in vacuo or in a current of hydrogen, but regains its yellow colour on cooling. At 300°, it decomposes into sodium carbonate and chromic oxide. When heated in air, it is converted into sodium chromate; when heated in chlorine it yields chromyl dichloride and chromic oxide; in hydrogen sulphide at about 240°, it yields the red, crystalline chromic sulphide—otherwise it resembles the decahydrate. When chromous acetate is treated with a 20 per cent. soln. of potassium carbonate, **potassium chromous carbonate,** $K_2CO_3.CrCO_3.3H_2O$, is formed in yellow, hexagonal prisms, which at first dissolve in water, but gradually polymerize, whether in soln. or in the solid state, and become less soluble. It is a powerful reducing agent, and decomposes water below 100°; when heated out of contact with air, it becomes brown, but regains its original colour on cooling; at about 280°, it decomposes. When heated in air, it is converted into potassium chromate. If the yellow, complex carbonate is suspended in water and treated with a current of carbon dioxide, or if the chromous acetate is treated with a dil. soln. of potassium carbonate, a less soluble, red double carbonate is formed; it is partially decomposed by water, and decomposes water at 100°. The carbonates of barium, strontium, and calcium have no action on chromous acetate, but magnesium hydrocarbonate converts chromous acetate into reddish-brown **magnesium chromous carbonate** which could not be obtained free from magnesium carbonate, and which decomposes water at 100°.

According to M. Z. Jovitschitsch, chromic hydroxide freed from all traces of alkali and ammonia, absorbs carbon dioxide from the atm. until the saturation limit corresponding with **chromic pentahydroxycarbonate,** $[Cr_2(OH)_5]_2CO_3.8H_2O$, is attained. This substance can be dried at 100° without losing carbon dioxide, but it is decomposed by acids. The graphic formula is supposed to be either



$$CO\begin{array}{l}\diagup O.Cr_2(OH)_5 \\ \diagdown O.Cr_2(OH)_5\end{array}.9H_2O, \quad \text{or} \quad O\begin{array}{l}\diagup Cr_2(OH)_4.O\diagdown \\ \diagdown Cr_2(OH)_4.O\diagup\end{array}CO.10H_2O.$$

According to H. Rose, alkali carbonates precipitate from soln. of chromic salts a pale green hydroxide containing more or less carbonate, which on standing becomes blue in daylight, and violet in artificial light. An excess of the precipitant dissolves the precipitate, and the soln. gives no precipitate when boiled; potassium or ammonium hydrocarbonate behaves similarly; but barium carbonate slowly precipitates hydrated chromic oxide completely from cold soln. J. N. von Fuchs made a similar observation with respect to calcium carbonate; and H. Demarçay, with respect to strontium and magnesium carbonates. K. F. W. Meissner, J. Lefort, and T. Parkman obtained basic chromic carbonates by the action of alkali or ammonium carbonate on a soln. of a chromic salt. M. Hebberling added that the freshly-formed precipitate is soluble in soln. of alkali carbonate or borax. The composition of the precipitate depends on the conditions; thus, K. F. W. Meissner gave $10Cr_2O_3.7CO_2.8H_2O$; J. J. Berzelius, $4Cr_2O_3.CO_2.H_2O$; and C. Langlois, $2Cr_2O_3.CO_2.6H_2O$.

T. Parkman dropped a cold, aq. soln. of chrome-alum into a soln. of sodium carbonate with constant stirring until the mixture had only a slight alkaline reaction. The unwashed, moist precipitate corresponded with **chromic oxydicarbonate,** $Cr_2O(CO_3)_2$. If the mixing be done in the reverse way, the precipitate is contaminated with sulphate. J. Lefort treated a violet soln. of a chromic salt with a moderate excess of sodium carbonate and, after washing and drying the product, obtained **chromic dioxycarbonate,** $Cr_2O_2(CO_3)$. It loses carbon dioxide at 300°. T. Parkman obtained a similar product by adding sodium carbonate to a boiling soln. of chrome alum; and W. Wallace by adding sodium or ammonium carbonate to a cold dil. soln. of chromic chloride. The washed precipitate was dried at ordinary temp.

O. T. Christensen prepared **chromic nitritopentamminocarbonate,** $[Cr(NH_3)_5(NO_2)]CO_3$, by triturating an excess of silver carbonate with the chloride of the series, and treating the filtrate with alcohol. The yellow, crystalline product could not be obtained pure. It is easily decomposed; is freely soluble in water; and the soln. gives the characteristic reactions of the carbonates.

According to N. J. Berlin, chromic carbonate dissolves sparingly in an aq. soln. of potassium carbonate, forming a pale-green soln. which separates on prolonged boiling. If chromic chloride is supersaturated with a conc. soln. of potassium carbonate, very little precipitate is redissolved; dissolution occurs on mixing more dil. soln. The soln. of hydrated chromic carbonate in a boiling soln. of potassium hydrocarbonate deposits on cooling a complex **potassium chromic carbonate** in pale green crystalline scales, while a soln. of potassium carbonate under similar conditions deposits a pulverulent complex salt on evaporation. A mineral associated with the serpentine and chromite of Dundas, Tasmania, was called **stichtite**—after R. Sticht—by W. F. Petterd,[2] and *chromobrugnatellite*, by L. Hezner. Its composition is that of a **magnesium chromic hydroxycarbonate,** $2MgCO_3.5Mg(OH)_2.2Cr(OH)_3.4H_2O$, like brugnatellite, with chromium in place of iron; or hydrotalcite with chromium in place of aluminium. The mineral occurs in micaceous scales of a lilac colour. The cleavage is good; the sp. gr. is 2·16; the refractive index, 1·542; it is optically uniaxial or feebly biaxial; the optical character is negative; and it is feebly pleochroic. Observations on the mineral were made by W. F. Foshag, L. Hezner, and A. Himmelbauer.

The mineral **beresowite,** *beresovite*, or *berezovite* was found by J. Samoiloff[3] in Berezov, Urals. associated with the galena and cerussite. It is a **lead carbonatochromate,** $6PbO.3CrO_3.CO_2$; and it occurs in deep red, birefringent plates of sp. gr. 6·69.

References.

[1] N. J. Berlin, *Stockholm Akad. Handl.*, 1, 1844; 65, 1845; *Journ. prakt. Chem.*, (1), **38**. 144, 1846; A. Moberg, *ib.*, (1), **44**. 328, 1848; O. T. Christensen, *ib.*, (2), **24**. 89, 1881; J. Lefort, *Journ. Pharm. Chim.*, (3), **14**. 15, 1848; *Compt. Rend.*, **27**. 269, 1848; M. Z. Jovitschitsch, *Monatsh.*, **34**. 225, 1913; *Helvetica Chim. Acta*, **3**. 46, 1920; *Compt. Rend.*, **158**. 872, 1914; G. Baugé, *ib.*, **122**. 474, 1896; **125**. 1177, 1897; **126**. 1566, 1898; **138**. 1219, 1904; *Sur quelques carbonates doubles du protoxyde de chrome* (*oxyde salin de chrome*), Paris, 1899; *Bull. Soc. Chim.*, (3), **19**. 107, 1898; (3), **19**. 107, 1898; (3), **31**. 782, 1904; *Ann. Chim. Phys.*, (7), **19**. 158, 1900; C. Langlois, *ib.*, (3), **48**. 502, 1856; H. Moissan, *ib.*, (5), **25**. 414, 1882; J. J. Berzelius, *Lehrbuch der chemie*, Dresden, **3**. 1086, 1848; T. Parkman, *Amer. Journ. Science*, (2), **34**. 321, 1862; *Chem. News*, **7**. 112, 122, 1863; W. Wallace, *B.A. Rep.*, 69, 1858; *Chem. Gaz.*, **16**. 410, 1858; *Journ. prakt. Chem.*, (1), **76**. 310, 1859; H. Rose, *Pogg. Ann.*, **83**. 143, 1851; J. Barratt, *Chem. News*, **1**. 110, 1860; M. Hebberling, *Chem. Centr.*, (3), **1**. 122, 1870; K. F. W. Meissner, *Gilbert's Ann.*, **60**. 366, 1818; J. N. von Fuchs, *Schweigger's Journ.*, **62**. 191, 1831; H. Demarçay, *Liebig's Ann.*, **11**. 241, 1834.

[2] W. F. Petterd, *Catalogue of the Minerals of Tasmania*, 167, 1910; L. Hezner, *Centr. Min.*, 569, 1912; A. Himmelbauer, *Tschermak's Mitt.*, (2), **32**. 135, 1913; W. F. Foshag, *Proc. U.S. Nat. Museum*, **58**. 147, 1921.

[3] J. Samoiloff, *Bull. Soc. Moscow*, 290, 1897.

§ 32. Chromium Nitrates

F. Allison and E. J. Murphy[1] reported the examination of the magneto-optic properties of a soln. of **chromous nitrate,** $Cr(NO_3)_2$. A. A. Hayes observed that a soln. of hydrated chromic oxide in an excess of nitric acid; or, according to H. Löwel, of a basic nitrate in that acid forms a soln. which is blue by reflected and red by transmitted light. According to J. R. Partington and S. K. Tweedy, a soln. of chromic hydroxide—freshly precipitated from chrome-alum in the cold, and washed with hot water—in cold $4N$-NHO_3 is green, but in a few days it becomes violet. When kept in a stoppered bottle, it deposits reddish-violet crystals of **chromic nitrate,** $Cr(NO_2)_3.12\frac{1}{2}H_2O$. The *hemipentacosihydrate* melts at 104° to 105°. J. M. Ordway found that the soln. furnishes purple, rhombic prisms of chromic nitrate, $Cr(NO_3)_3.9H_2O$. J. R. Partington and S. K. Tweedy obtained the crystals of the enneahydrate by allowing a soln. of violet chromic chloride in nitric acid to crystallize in a vacuum desiccator. The *enneahydrate* melts at 36·5°, and decomposes at 100°. It is soluble in alcohol. J. R. Partington and S. K. Tweedy gave 66° to 66·5° for the m.p., and there is no sign of a transition at this temp. to a second hydrate. O. M. Halse said that a soln. of hydrated chromic oxide in dil. nitric acid, when evaporated very slowly, deposits violet crystals of the *hemipentadecahydrate*, $2Cr(NO_3)_3.15H_2O$, which melt at 100°, and decompose during dehydration; but J. R. Partington and S. K. Tweedy said that O. M. Halse's salt is really the hemipentacosihydrate. M. Z. Jovitschitsch found that by dissolving chromic oxide in hot, conc. nitric acid, of sp. gr. 1·4, the soln. on crystallization furnish dark brown, monoclinic prisms of the hemipentadecahydrate, $2Cr(NO_3)_3.15H_2O$, with the axial ratios $a:b:c=1{\cdot}4250:1:1{\cdot}1158$, and $\beta=93°\ 10'$. In contact with dry air, the grey coloured *hemienneahydrate*, $2Cr(NO_3).9H_2O$, is formed. The crystals are red by transmitted light; they are not changed by air; and dissolve in water, and alcohol. M. Z. Jovitschitsch found that the evaporation of a nitric acid soln. of chromic oxide yields a dark brown mass which, when dissolved in water and the soln. evaporated, furnishes a dark green, crystalline mass of anhydrous chromic nitrate, $Cr(NO_3)_3$. This is stable in light, and takes up moisture from the air to form the *trihydrate*, $Cr(NO_3)_3.3H_2O$.

I. Traube gave for the sp. gr. of the violet aq. soln. with 3·389, 7·550, 16·536, and 29·082 per cent. of $Cr(NO_3)_3$, respectively 1·02699, 1·06252, 1·14602, and 1·28163 at 15° when the mol. soln. vol. are respectively 47·9, 50·2, 53·7, and 57·7. C. Montemartini and L. Losana studied the viscosity of the soln. H. C. Jones and F. H. Getman measured the sp. gr. and the f.p. of soln. of chromic nitrate. For soln. with 0·0934, 0·3736, 1·1208, and 1·8680, the respective sp. gr. were 1·021, 1·069, 1·203, and 1·334; and the respective f.p. were —0·280°, —2·493°, —11·57°, and —29·50°. J. R. Partington and S. K. Tweedy found the viscosities, η dyne per cm. of soln. containing W grms. of $Cr(NO_3)_3$ per 100 grms. of water to be:

W . .	29·11	23·62	15·07	7·16	3·55
η 18° . .	0·01948	0·01669	0·01373	0·01172	0·01102
η 25° . .	0·01498	0·01122	0·01050	0·00999	0·00993

C. Montemartini and L. Losana observed a break in the expansion curve of soln. of chromium nitrate. L. R. Ingersoll found for Verdet's constant for the electromagnetic rotatory power for light of wave-length 0·8, 1·0, and 1·25μ, respectively 0·0066, 0·0041, and 0·0025 for soln. of chromic nitrate of sp. gr. 1·087. W. N. Hartley found that two violet soln. of the nitrate showed absorption bands respectively between 5880 and 5570, and 5650 and 5070. The violet soln. becomes green when heated. According to O. Knoblauch, the absorption spectrum of the soln. has a faint band at 6670, and a band between 6160 and 5770, with a small absorption at 513. When the soln. is diluted the band moves to 6180 to 5920. J. M. Hiebendaal observed a band between 6130 and 5320, and absorption from 4540. The addition of ammonium chloride weakens the band, and produces a narrow band at 6370; in alcoholic soln., there is a narrow band at 6370; a band between 6550 and 5350, with a maximum between 6130 and 5500; and absorption from 4600. A. Étard found bands between 6780 and 6700, and between 6540 and 6330. The spectrum was also examined by A. Byk and H. Jaffe. The electrical conductivity of soln. of the nitrate was measured by H. C. Jones and co-workers, and by N. Bjerrum. H. C. Jones and C. A. Jacobson found the mol. conductivity, μ mhos, of soln. with a mol of the salt in v litres between 0° and 35°; and A. P. West and H. C. Jones, and E. J. Shaeffer and H. C. Jones, between 35° and 65°:

	v	2	8	16	32	128	512	1024	2048
μ	0°	92·9	125·3	138·3	147·6	158·8	201	216	224
	10°	119·5	163·2	180·9	193·9	212	270	292	315
	25°	164·9	228	254	275	305	395	440	467
	35°	192·3	279	312	343	417	504	549	595
	65°	297	445	504	560	705	869	539	1032
α	0°	41·4	55·9	61·6	65·8	70·8	89·7	96·5	100·0
	35°	38·0	46·6	52·2	56·8	63·7	83·6	93·4	100·0

The values for the percentage ionization, α, were calculated by H. C. Jones and C. A. Jacobson; and H. M. Vernon calculated the degree of ionization from the colour. N. Bjerrum calculated the percentage hydrolysis, 100β, and the hydrolysis constant K for $Cr(NO_3)_3+H_2O \rightleftharpoons Cr(NO_3)_2OH+HNO_3$, from $K=[H]^{\cdot}[Cr(OH)^{\cdot\cdot}]/[Cr^{\cdot\cdot\cdot}]=m\beta^2/(1-\beta)$, from the conductivity, μ mhos, for soln. with m mols per litre at 19·8°:

m	0·02	0·01	0·005	0·0025	0·00125	0·00625
μ	265·7	299·1	316·0	345·2	374·8	406·5
100β	5·0	7·2	9·0	14·2	18·6	26·0
K	$0{\cdot}0_452$	$0{\cdot}0_456$	$0{\cdot}0_445$	$0{\cdot}0_449$	$0{\cdot}0_453$	$0{\cdot}0_457$

so that the average value of K is 0·00054. G. Herrmann said that his attempt to reduce a soln. of chromic nitrate, electrolytically, *wie nicht anders zu erwarten war*, were unsuccessful. L. A. Welo measured the magnetic susceptibility of the solid and molten hydrate, $Cr(NO_3)_3.3{\cdot}4H_2O$, and the results are summarized in Fig. 86. The Curie points, $C=\chi(T-\theta)$, are for the solid and liquid states, $C_s=1{\cdot}90$; $C_l=1{\cdot}50$; $\theta_s=-85°$; and $\theta_l=5°$. P. Philipp found the magnetic susceptibility to be $24{\cdot}09\times10^{-6}$ and $22{\cdot}75\times10^{-6}$ for soln. respectively of sp. gr. 1·3295 and 1·02706.

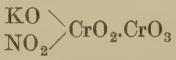
According to J. M. Ordway, when alkali hydroxide is added to a soln. of chromic nitrate, chromic hydroxide is precipitated. The precipitate appears when more than two-thirds of the acid has been neutralized. This proves that nitric acid can dissolve more chromic hydroxide than corresponds with the normal nitrate. C. Montemartini and L. Losana studied the e.m.f. of the soln. N. Bjerrum and C. Fourholt determined the masked hydroxide, $Cr(H_2O)_6^{\cdots}$, by precipitation as cæsium alum. With soln. of chromic nitrate they obtained the results indicated in Table V.

TABLE V.—THE HYDROLYSIS OF SOLUTIONS OF CHROMIC NITRATE.

M-Molar Soln.	Eq. of base present.	Days heated to 75°.	Per cent. latent chromium.	Masked OH-radicles per 100 Cr-atoms.	Masked OH-radicles per Cr-atom in latent basic Cr.
0·01	—	3 to 4	17·6	20	1·14
0·05	—	7	20·1	25	1·24
0·01	—	5	31·4	40	1·27
0·05	0·5	1 to 5	47·3	57	1·21
0·05	1·0	2 to 9	67·0	103	1·54
0·05	2·0	2 to 3	89·0	179	2·01

A. A. Hayes observed that when a soln. of an excess of chromic oxide in nitric acid is evaporated, it does not furnish crystals, but dries up to a gummy, fissured mass which appears dark green by reflected and transmitted light. J. J. Berzelius, and F. Brandenburg made some observations on this subject. H. Löwel assumed that the green soln. obtained by dissolving hydrated chromic oxide in hot nitric acid contains **chromic hydroxydinitrate,** $Cr(OH)(NO_3)_2$. J. M. Ordway obtained what he regarded as the *hexahydrate*, $Cr(OH)(NO_3)_2.6H_2O$, by keeping crystals of the normal nitrate on the water-bath. The dark green residue is soluble in water, forming a dark brown liquid which contains chromic nitrate and chromate. H. Schiff said that by digesting the warm nitric acid soln. for a long time, the precipitate which is formed contains Cr_2O_3 and 1 or $2N_2O_5$. M. Siewert also said that a sat. blue soln. of hydrated chromic oxide in cold nitric acid contains $Cr(OH)(NO_3)_2$; and the green soln. in hot nitric acid, $2Cr_2O_3.3N_2O_5$ or $Cr(OH)_3Cr(NO_3)_3$. J. M. Ordway assumed that the sat. soln. of hydrated chromic oxide in nitric acid contains $8Cr_2O_3.3N_2O_5$, or $3Cr_2O_3.5Cr(NO_3)_3$. By treating chromic acid, or chromates with nitric acid, F. Brandenburg, H. Moser, and K. F. W. Meissner obtained chromic acid associated with nitric acid. J. E. Howard and W. H. Patterson examined the effect of chromic nitrate on the critical soln. temp. of water and isobutyric acid. For V. Ipatieff and B. Mouromtseff's observations on the action of hydrogen under press., *vide supra*, hydrated chromic oxide.

L. Darmstädter [2] heated potassium chromate with two parts of conc. nitric acid and obtained crimson tabular crystals of what he regarded as **potassium nitritodichromate,** $KCr_2O_5(NO_2)$, or



$$\left.\begin{matrix}KO\\NO_2\end{matrix}\right\rangle CrO_2.CrO_3$$

and an excess of nitric acid was said to convert it into **potassium nitritotrichromate,** $KCr_3O_9(NO)_2$. The aq. soln. furnishes potassium dichromate. The salt melts to a dark brown liquid, and at the same time gives off red fumes. G. N. Wyrouboff, and G. C. Schmidt questioned the existence of these salts—*vide supra.*

H. Schiff treated the hydroxydichloride with nitric acid, and on evaporating the soln. obtained **chromic dichloronitrate,** $CrCl_2(NO_3)$, in hygroscopic plates. When heated, it decomposes: $2CrCl_2(NO_3)=2NO_2Cl+Cr_2O_2Cl_2$. The sol. has an acidic reaction; and the salt is soluble in alcohol. If the soln. of the dihydroxychloride in dil. nitric acid be evaporated, **chromic hydroxychloronitrate,** $Cr(OH)(NO_3)Cl$, is formed as a hygroscopic mass. H. Schiff also obtained **chromic sulphatonitrate,** $Cr(NO_3)SO_4$, as a green, hygroscopic mass, by the action of nitric acid on chromic oxydisulphate; and **chromic tetranitratosulphate,** $Cr_2(NO_3)_4SO_4$, as a brown soluble, hygroscopic mass by evaporating a soln. of the basic sulphate in nitric acid at 80°–90°.

S. M. Jörgensen [3] prepared **chromic hexamminotrinitrate,** $[Cr(NH_3)_6](NO_3)_3$, by reducing a soln. of potassium dichromate first by alcohol and hydrochloric acid, and then by the addition of zinc; adding ammonium chloride and ammonia; and allowing the mixture to stand 24 hrs. W. R. Lang and C. M. Carson, and O. T. Christensen treated with nitric acid the product of the action of liquid ammonia on anhydrous chromic chloride. The orange-yellow plates dissolve in water—100 parts of water dissolve 2·5 to 3 parts of the salt. A. Werner and A. Miolati found soln. with a mol of salt in 125, 250, 500, 1000, and 2000 litres at 25° had the respective conductivities $\mu=341{\cdot}2$, 374·1, 401·1, 425·3, and 444·2 mhos. H. J. S. King also measured the electrical conductivity of soln. of this salt. E. Rosenbohm gave $20{\cdot}42\times10^{-6}$ mass unit for the magnetic susceptibility. The salt is decomposed by boiling water; and the aq. soln. gives precipitates with hydrobromic, hydriodic, hydrofluosilicic, hydrochloroplatinic, and hydrochloroauric acids, potassium chromate, dichromate, triiodide, and ferricyanide, and sodium dithionate. F. Ephraim and W. Ritter observed that while the hexammine absorbs ammonia gas at low temp., the dissociation curves show no breaks corresponding with the formation of definite ammines. A. Benrath found that in the presence of conc. nitric acid, $[Cr(NH_3)_6](NO_3)_3.HNO_3$ is formed. S. M. Jörgensen also prepared the **hydrotetranitrate,** and a chloroplatinate. P. Pfeiffer prepared **chromic terethylenediaminotrinitrate,** $[Cr\ en_3](NO_3)_3$. O. T. Christensen obtained **chromic aquopentamminotrinitrate,** $[Cr(NH_3)_5(H_2O)](NO_3)_3$, as in the case of the bromide or iodide. The yellowish-red salt is freely soluble in water; it loses water at 100°; and detonates at a higher temp. A. Benrath found that in the presence of nitric acid $[Cr(NH_3)_6](NO_3)_3$ is formed. P. Pfeiffer prepared the **hydrotetra-**

nitrate. P. Pfeiffer treated the hydroxyaquotetramminodithionate with conc. nitric acid, and obtained **chromic diaquotetramminohydrotetranitrate,** $[Cr(NH_3)_4(H_2O)_2](NO_3)_4H$, as an orange powder. E. H. Riesenfeld and F. Seemann obtained red crystals of **chromic triaquotriamminodichloronitrate,** $[Cr(NH_3)_3(H_2O)_3]Cl_2(NO_3)$, by treating an aq. soln. of the trichloride with conc. nitric acid, and **chromic nitratodiaquotriamminodinitrate,** $[Cr(NH_3)_3(H_2O)_2(NO_3)](NO_3)_2$, from a soln. of chromium triamminotetroxide in conc. nitric acid. P. Pfeiffer and W. Osann prepared **chromic tetraquodipyridinotrinitrate,** $[CrPy_2(H_2O_4)](NO_3)_3$. M. Kilpatrick studied **chromic hexaureatrinitrate,** $[Cr(NH_2.CO.NH_2)_6](NO_3)_3$. R. Weinland and W. Hübner studied other complexes with organic radicles.

O. T. Christensen obtained **chromic nitritopentamminodinitrate,** $[Cr(NH_3)_5(NO_2)](NO_3)_2$, by the action of ammonium nitrate on a soln. of the chloride. The yellow octahedral crystals are sparingly soluble in water 100 parts of which dissolve 0·67 part of the salt. The salt detonates when heated. F. Ephraim and W. Ritter observed that **chromic aquopentamminotrinitrate,** $[Cr(NH_3)_5(H_2O)](NO_3)_3$, absorbs ammonia gas at a low temp., the decomposition curve shows that possibly a monammine is formed. Ammonia converts the salt into the hydroxypentamminonitrate, $[Cr(NH_3)_5(OH)](NO_3)_3$. F. Ephraim and W. Ritter found that ammonia gas is absorbed by chromic nitritopentamminonitrate, but the decomposition curve shows no breaks. H. J. S. King obtained **chromic hydroxypentamminodinitrate,** $[Cr(NH_3)_5(OH)](NO_3)_2.\frac{1}{2}H_2O$, by the action of the hydroxide on a soln. of ammonium nitrate, and precipitation with alcohol and ether. He gave for the conductivity, μ mhos, of a mol of the salt in v litres,

v	32	64	128	256	512	1024	2048
μ 0°	106·4	115·7	124·7	132·0	138·9	141·4	152·7
μ 25°	201·5	219·4	233·6	244·3	254·2	260·8	279·9

A. Werner and J. von Halban prepared **chromic nitratopentamminodinitrate,** $[Cr(NH_3)_5(NO_3)](NO_3)_2$, by the action of fuming nitric acid on chromic thiocyanatopentamminonitrate, or of nitric acid on aquopentamminohydroxide. The pale flesh-coloured powder is sparingly soluble in water, and the soln. is liable to decompose. A. Benrath found that with nitric acid, $[Cr(NH_3)_5(H_2O)](NO_3)_2$ may be formed. A. Werner and J. von Halban prepared **chromic nitratopentamminodiiodide,** $[Cr(NH_3)_5(NO_3)]I_2$, by shaking up the nitrate with solid potassium iodide and water. E. H. Riesenfeld and F. Seemann prepared **chromic nitratodiaquotriamminodinitrate,** $[Cr(NH_3)_3(H_2O)_2(NO_3)](NO_3)_2$, by the action of conc. nitric acid on the cold on chromic triamminotetroxide. A. Hiendlmayr prepared **chromic fluopentamminodinitrate,** $[Cr(NH_3)_5F](NO_3)_2$, by the action of calcium nitrate on the difluoride. S. M. Jörgensen prepared **chromic chloropentamminodinitrate,** $[Cr(NH_3)_5Cl](NO_3)_2$, by the action of nitric acid on a cold soln. of the chloride of the series. The carmine-red octahedra are soluble in water; at 17·5°, 100 parts of water dissolve 1·4 parts of salt. A. Werner and A. Miolati found that a mol of the salt in 125, 250, 500, 1000, and 2000 litres of water at 25° have the electrical conductivities μ=250·2, 265·9, 279·0, 288, 299·1 mhos respectively. P. T. Cleve, and S. M. Jörgensen prepared **chromic chloroaquotetramminodinitrate,** $[Cr(NH_3)_4(H_2O)Cl](NO_3)_2$, by the action of nitric acid on the chloride of the series. The carmine-red, or purple-red rhombohedral crystals lose no water over sulphuric acid; at 100°, the salt blackens. A. Werner and A. Miolati found that the soln. of a mol of the salt in 125, 250, 500, 1000, and 2000 litres of water at 25° has the electrical conductivity 206·5, 226·4, 244·7, 260·3, and 282·5 mhos respectively. S. M. Jörgensen prepared violet, octahedral crystals of **chromic bromopentamminodinitrate,** $[Cr(NH_3)_5Br](NO_3)_2$, by the action of nitric acid on the chloride of the series; and also reddish-violet crystals of **chromic iodopentamminodinitrate,** $[Cr(NH_3)_5I](NO_3)_2$. A. Werner and J. von Halban prepared **chromic thiocyanatopentamminodinitrate,** $[Cr(NH_3)_5(SCy)](NO_3)_2$.

S. Guralsky prepared **chromic dibromoaquotriamminonitrate,** $[Cr(NH_3)_3$-

$(H_2O)Br_2]NO_3$; P. Pfeiffer and W. Osann, **chromic dihydroxydiaquodipyridinonitrate,** $[CrPy_2(H_2O)_2(OH)_2]NO_3$; P. Pfeiffer and T. G. Lando, and A. Werner **chromic cis-dichlorobisethylenediaminonitrate,** $[Cr\,en_2Cl_2]NO_3$, and P. Pfeiffer and P. Koch, the **trans-salt.** A. Werner obtained greyish-blue needles of **chromic dichlorodiaquotriamminonitrate,** $[Cr(NH_3)_3(H_2O)_2Cl_2]NO_3$, by the action of nitric acid on the chloride of the series. Y. Shibata measured the absorption spectrum. P. Pfeiffer and M. Tapuach prepared **chromic dichlorodiaquodipyridinonitrate,** $[CrPy_2(H_2O)_2Cl_2]NO_3.2H_2O$; P. Pfeiffer and M. Tapuach, **chromic trans-dibromobisethylenediaminonitrate,** $[Cr\,en_2Br_2]NO_3$; **chromic dibromodiaquodipyridinonitrate,** $[CrPy_2(H_2O)_2Br_2]NO_3$; P. Pfeiffer and M. Tilgner, **chromic dithiocyanatotetramminonitrate,** $[Cr(NH_3)_4(SCy)_2]NO_3$; P. Pfeiffer and P. Koch, **chromic cis-dithiocyanatobisethylenediamine,** $[Cr\,en_2(SCy)_2]NO_3$; and P. Pfeiffer, the **trans-salt.** P. Pfeiffer and S. Basci also obtained **chromic oxalatotetramminonitrate,** $[Cr(NH_3)_4(C_2O_4)]NO_3.H_2O$.

S. M. Jörgensen prepared rose-red or pale carmine-red aggregates of needles of **chromic hydroxydecamminopentanitrate,** $[Cr_2(OH)(NH_3)_{10}](NO_3)_5$, by the action of nitric acid on the chloride or bromide of the series. The rhodo-salt so obtained is sparingly soluble in water. S. M. Jörgensen also prepared the erythro-salt in an analogous way. He also obtained **chromic trihydyroxyaquohexamminotrinitrate,** $[Cr_2(OH)_3(H_2O)(NH_3)_6](NO_3)_3$, in pale carmine-red needles sparingly soluble in cold water; and the soln. is liable suddenly to precipitate hydrated chromic oxide. The salt decomposes at 100°; and over sulphuric acid, it gives off a mol. of water. R. F. Weinland and E. Gussmann prepared **chromic dihydroxyhexacetatotripyridinonitrate,** $[Cr_3(CH_3COO)_6Py_3(OH)_2]NO_3.5H_2O$; and P. Pfeiffer and W. Vorster, **chromic hexahydroxysexiesethylenediaminohexanitrate,** $[Cr_4(OH)_6en_6](NO_3)_6.6H_2O$.

P. T. Cleve reported the salts **chromic diamminodihydroxydinitrate,** $Cr(OH)_2(NO_3)_2(NH_3)_2.\frac{1}{2}H_2O$; **chromic diamminopentahydroxynitrate,** $Cr_2(OH)_5(NO_3)(NH_3)_2.nH_2O$; and also **ammonium chromic heptamminoctonitrate,** $2Cr(NO_3)_3.2NH_4NO_3.(NH_3)_7.4\frac{1}{2}H_2O$; and **chromic oxalatohemienneamminonitrate,** $Cr(NO_3)(C_2O_4).4\frac{1}{2}NH_3.1\frac{1}{2}H_2O$. M. Z. Jovitschitsch dissolved a gram of hydrated chromic oxide in enough nitric acid, diluted the liquid to 25 c.c., added the same vol. of ammonia, and found that alcohol precipitated a soluble, scarlet mass of **chromic dioxyheptamminotrinitrate,**

$$\begin{array}{l}(NH_3)_2{=}Cr.O.NH_3.Cr{=}(NO_3)_2\\(NH_3)_2{=}\dot{C}r.O.NH_3.\dot{C}r(NO_3)(NH_3)\end{array}\quad 10H_2O$$

R. Weinland and co-workers prepared complex salts of the nitrate with pyridine, *o*-toluidine, guanidine, and aniline.

References.

[1] J. M. Ordway, *Amer. Journ. Science*, (2), **9**. 30, 1850; (2), **26**. 202, 1858; A. A. Hayes, *ib.*, (1), **14**. 136, 1828; (1), **20**. 409, 1831; F. Brandenburg, *Schweigger's Journ.*, **13**. 274, 1815; *Scherer's Ann.*, **3**. 61, 1820; *Ann. Gén. Science Phys.*, **1**. 85, 1819; J. J. Berzelius, *Schweigger's Journ.*, **22**. 53, 1818; *Pogg. Ann.*, **1**. 34, 1824; *Ann. Chim. Phys.*, (2), **17**. 7, 1821; H. Moser, *Chemische Abhandhung über das Chrom*, Wien, 1824; *Schweigger's Journ.*, **42**. 99, 1824; K. F. W. Meissner, *Gilbert's Ann.*, **60**. 366, 1818; J. E. Howard and W. H. Patterson, *Journ. Chem. Soc.*, **129**. 2791, 1927; G. Herrmann, *Ueber die elektrolytische Darstellung von Chromosalzen.* München, 1909; V. Ipatieff and B. Mouromtseff, *Ber.*, **60**. B, 1980, 1927; L. R. Ingersoll, *Journ. Amer. Opt. Soc.*, **6**. 663, 1922; C. Montemartini and L. Losana, *Notiz. Chim. Ind.*, **2**, 551, 1927; M. Kilpatrick, *Journ. Amer. Chem. Soc.*, **50**. 358, 1928; F. Allison and E. J. Murphy, *ib.*, **52**. 3796, 1930; J. R. Partington and S. K. Tweedy, *Journ. Chem. Soc.*, 1142, 1926; M. Siewert, *Liebig's Ann.*, **126**. 99, 1863; H. Schiff, *ib.*, **124**. 170, 1862; H. Löwel, *Journ. Pharm. Chim.*, (3), **4**. 401, 1845; M. Z. Jovitschitsch, *Monatsh.*, **30**. 47, 1909; **33**. 9, 1912; **34**. 225, 1913; *Helvetica Chim. Acta*, **3**. 46, 1920; *Compt. Rend.*, **158**. 872, 1914; A. Étard, *ib.*, **120**. 1057, 1895; H. M. Vernon, *Chem. News*, **66**. 104, 114, 141, 152, 1892; O. M. Halse, *Chem. Ztg.*, **36**. 962, 1912; I. Traube, *Zeit. anorg. Chem.*, **8**. 35, 1895; A. Benrath, *ib.*, **177**. 286, 1928; N. Bjerrum, *ib.*, **119**. 66, 1921; *Studien over basishe Kromiforbindelser*, Kopenhagen, 1908; *Ber.*, **39**. 1597, 1906; *Danske Vid. Selsk. Skr.*, (7), **4**. 79, 1907; *Zeit. phys. Chem.*, **59**.

369, 1907 ; **73**. 723, 1910 ; N. Bjerrum and C. Faurholt, *ib.*, **130**. 584, 1927 ; H. C. Jones and F. H. Getman, *ib.*, **49**. 426, 1904 ; H. C. Jones and C. A. Jacobson, *Amer. Chem. Journ.*, **40**. 355, 1908 ; E. J. Shaeffer and H. C. Jones, *ib.*, **49**. 207, 1913 ; A. P. West and H. C. Jones, *ib.*, **44**. 508, 1910 ; W. N. Hartley, *Trans. Roy. Dublin Soc.*, (2), **7**. 253, 1900 ; J. M. Hiebendaal, *Onderzoek over eenige absorptiespectra*, Utrecht, 1873 ; O. Knoblauch, *Wien. Ann.*, **43**. 738, 1891 ; L. A. Welo, *Nature*, **124**. 575, 1929 ; A. Byk and H. Jaffe, *Zeit. phys. Chem.*, **68**. 323, 1910 ; P. Philipp, *Untersuchungen über Magnetisierungszahlen von Salzen der Eisengruppe und ihre Abhängigkeit von der Konzentration*, Rostock, 1914.

[2] L. Darmstädter, *Ber.*, **4**. 117, 1871 ; G. C. Schmidt, *ib.*, **25**. 2917, 1892 ; G. N. Wyrouboff, *Bull. Soc. Chim.*, (2), **35**. 162, 1881 ; H. Schiff, *Liebig's Ann.*, **124**. 174, 1862.

[3] F. Ephraim and W. Ritter, *Helvetica Chim. Acta*, **11**. 848, 1928 ; Y. Shibata, *Journ. Coll. Science Japan*, **41**. 6, 1919 ; S. M. Jörgensen, *Journ. prakt. Chem.*, (2), **20**. 134, 1879 ; (2), **25**. 90, 337, 1882 ; (2), **30**. 6, 1884 ; (2), **42**. 209, 1890 ; (2), **44**. 65, 1891 ; (2), **45**. 248, 1892 ; H. J. S. King, *Journ. Chem. Soc.*, **125**. 1329, 1924 ; **127**. 2100, 1925 ; O. T. Christensen, *ib.*, (2), **23**. 41, 1881 ; (2), **24**. 81, 1881 ; *Zeit. anorg. Chem.*, **4**. 229, 1893 ; P. Pfeiffer and W. Vorster, *ib.*, **58**. 294, 1908 ; P. Pfeiffer, *ib.*, **24**. 296, 1900 ; **29**. 134, 1901 ; **56**. 291, 1907 ; *Ber.*, **40**. 3133, 1907 ; P. Pfeiffer and W. Osann, *ib.*, **40**. 4034, 1907 ; W. Osann, *Zur Chemie der Dipyridinchromsalze*, Zürich, 1905 ; P. Pfeiffer and M. Tilgner, *Zeit. anorg. Chem.*, **55**. 368, 1907 ; P. Pfeiffer and S. Basci, *Ber.*, **38**. 3599, 1905 ; S. Basci, *Beitrag zur Chemie ammoniakalischer Chromsalze*, Zürich, 1907 ; T. G. Lando, *Beitrag zur Kenntnis der Aquo- und Diacido-diaethylendiaminchromsalze*, Zürich, 1904 ; P. Pfeiffer and T. G. Lando, *Ber.*, **37**. 4281, 1904 ; P. Pfeiffer and P. Koch, *ib.*, **37**. 4287, 1904 ; P. Koch, *Beitrag zur Stereoisomerie der Chromsalze*, Zürich, 1905 ; M. Tapuach, *Zur Kenntnis der Hydratisomerie bei Di- und Trihalogenochromsalzen*, Zürich, 1907 ; P. Pfeiffer and M. Tapuach, *Ber.*, **39**. 1889, 1906 ; A. Werner and A. Miolati, *Zeit. phys. Chem.*, **14**. 516, 1894 ; A. Werner and J. von Halban, *Ber.*, **39**. 2670, 1906 ; A. Werner, *ib.*, **39**. 2665, 1906 ; **43**. 2293, 1910 ; **44**. 3135, 1910 ; S. Guralsky, *Ueber Di- und Triamminchromisalze*, Zürich, 1909 ; W. R. Lang and C. M. Carson, *Journ. Amer. Chem. Soc.*, **26**. 414, 1904 ; P. T. Cleve, *Oefvers. Akad. Förh.*, 176, 1861 ; *Svenska Akad. Handl.*, **6**. 4, 1865 ; E. Rosenbohm, *Zeit. phys. Chem.*, **93**. 693, 1919 ; M. Z. Jovitschitsch, *Monatsh.*, **34**. 225, 1913 ; E. H. Riesenfeld and F. Seemann, *Ber.*, **42**. 4222, 1909 ; F. Seemann, *Ueber Chromi-aquo-Triammine*, Freiburg, 1910 ; M. Kilpatrick, *Journ. Amer. Chem. Soc.*, **50**. 358, 1928 ; R. F. Weinland and E. Gussmann, *Zeit. anorg. Chem.*, **67**. 167, 1910 ; R. Weinland and W. Hübner, *Zeit. anorg. Chem.*, **178**. 275, 1929 ; A. Hiendlmayr, *Beiträge zur Chemie der Chrom- und Kobalt-Ammoniake*, Freising, 1907 ; A. Benrath, *Zeit. anorg. Chem.*, **177**. 286, 1928 ; R. Weinland and J. Lindner, *ib.*, **190**. 285, 1930 ; R. Weinland and W. Hübner, *ib.*, **178**. 275, 1929.

§ 33. Chromium Phosphates

A. Moberg [1] added sodium dihydrophosphate to a soln. of chromous salt and obtained a blue amorphous precipitate of **chromous phosphate,** $Cr_3(PO_4)_2.nH_2O$, which rapidly turns green on exposure to air forming, according to H. Moissan, a chromic salt. The precipitate is soluble in acids—*e.g.* in acetic, tartaric, and citric acids. It is insoluble in water, and a little soluble in water containing carbon dioxide. When heated under press. at 100° it remains amorphous. C. U. Shepard found it occurring naturally in green masses ; and he called it *phosphorchromite*. A. Colani was unable to prepare **chromous metaphosphate,** $Cr(PO_3)_2$, by the action of fused metaphosphoric acid on chromium or chromous salts, although the method is applicable for the corresponding ferrous salt.

L. N. Vauquelin [2] found that hydrated chromic oxide dissolves in an aq. soln. of phosphoric acid, forming an uncrystallizable, emerald-green liquid. When a soln. of chromic chloride is mixed with potassium phosphate, a green precipitate is obtained, which appears bluish-black after ignition, and yields a greenish-brown powder. If a hot soln. of chrome-alum is treated with an excess of sodium hydrophosphate, hydrated chromic phosphate is precipitated, and when this is heated, it yields brown **chromic orthophosphate,** $CrPO_4$. A. F. Joseph and W. N. Rae observed that the brown anhydrous salt is formed when any of the hydrates is heated to dull redness—*vide infra*. It is very resistant towards chemical agents being insoluble in hydrochloric acid or aqua regia, and only attacked by sulphuric acid when nearly boiling. It is then converted into an earthy-coloured powder, insoluble in water and acids, which appears to be a compound of chromium phosphate and sulphate of indefinite composition. The anhydrous phosphate requires calcining with lime before it can be dissolved by alkali-lye. W. Lapraik found that a soln. of hydrated chromic oxide in phosphoric acid shows an absorption band in the green. H. T. S. Britton studied the electrometric titration of soln. of chromic sulphate with sodium phosphate. W. J. Sell dialyzed a soln. of chromic phosphate in an ammoniacal soln. of ammonium hydrophosphate, and obtained **colloidal chromic phosphate.** N. R. Dhar and co-workers studied the adsorption of calcium salts by colloidal chromic phosphate. The electrical conductivity of the sol shows that there are no free ions exist in soln., and this is confirmed by the fact that the sol coagulates. J. A. Hedvall and J. Heuberger found that chromic phosphate begins to react with baryta: $2CrPO_4+3BaO=Ba_3(PO_4)_2+Cr_2O_3$ at 342°; with strontia at 464°; and with lime at 517°.

Some green pigments are composed essentially of chromic phosphate. Thus, J. Arnaudon obtained a green pigment by heating to 170°–180° for half an hour a mixture of 128 parts of normal ammonium phosphate and 149 parts of potassium dichromate, and washing the product with hot water. E. Mathieu-Plessy, and G. Köthe, by boiling 10 kgrms. of potassium dichromate in 100 litres of water, and 30 litres of a soln. of monocalcium phosphate, and 2·5 kgrms. of cane sugar; and G. Schnitzer, by melting 36 grms. of crystalline sodium phosphate, 15 grms. of potassium dichromate, and 6 grms. of tartaric acid and washing the product with cold hydrochloric acid, and then with hot water. J. Dingler employed a similar process. A. Carnot boiled a mixture of an alkali chromate, and sodium thiosulphate in the presence of phosphoric acid. W. Muthmann and H. Heramhof recommended chromic phosphate as a more stable pigment than chromic oxide for high temp. work.

C. F. Rammelsberg showed that when a cold soln. of sodium dihydrophosphate is added drop by drop to an excess of chrome-alum, the precipitate is lavender or violet, amorphous *hexahydrate;* and if this be allowed to remain in contact with the soln. for, say, 48 hrs., it furnishes the dark violet, crystalline hexahydrate. It may be washed by decantation, filtered, and dried in air. If the chrome-alum be not in excess, a violet powder is formed which does not crystallize if allowed to stand for days. H. Schiff added that this compound is formed only in acidic soln. when the chrome-alum is in excess. The triclinic crystals have a sp. gr. of 2·121 at 14°; A. F. Joseph and W. N. Rae gave 2·12 for the sp. gr. of the hexahydrate at 32·5°. All the hydrates at a low red-heat form the black anhydride, which has a sp. gr. 2·94 at 32·5°. The sp. gr. increases during a prolonged ignition owing to the loss of phosphoric oxide. The following data denote respectively the percentage losses and sp. gr.: heated over a bunsen burner for 1 hr., 1·2, and 3·16, and for 3 hrs., 2·4, and 3·29; heated 36 hrs. at 1100°, 4·4, and 3·42; and when heated 36 hrs. in a draught-furnace, 9·8, and 3·66; and for 50 hrs., 11·7, and 3·78. A. Étard stated that the hexahydrate lost 3·5 mols. of water at 100°. H. Schiff said that the hexahydrate forms a green pseudomorph at 100°, and loses 3 mols. of water, and a fourth mol. is not all expelled when kept for 4 days at this temp. H. Schiff said that when the hexahydrate is boiled with acetic anhydride it forms a green salt. C. F. Rammelsberg said that a green phosphate is formed if the chrome-alum soln. be added to an excess of a soln. of sodium dihydrophosphate. C. L. Bloxam acidified the soln. with acetic acid, and boiling the mixture—*vide infra;* and A. Carnot worked with a boiling acid soln. in the presence of sodium acetate—if a chromate soln. is used, it is reduced to the chromic state by the simultaneous addition of sodium thiosulphate. There is some difference of opinion as to the composition of the green hydrate dried at 100°. C. L. Bloxam, and A. Étard regarded it as a *hemipentahydrate;* and C. F. Rammelsberg, and A. Carnot, as a *trihydrate;* while H. Schiff found that the salt obtained by the action of boiling acetic anhydride on the violet hexahydrate is the green *dihydrate.* A. F. Joseph and W. N. Rae who observed no evidence of the existence of the hemipentahydrate or of the trihydrate, but, in agreement with H. Schiff, they observed the formation of the dihydrate, and found that the dehydration does not proceed any further if the boiling be prolonged. If the dry hexahydrate be heated, A. F. Joseph and W. N. Rae observed that the first break occurs when the dihydrate appears. The dihydrate has a sp. gr. of 2·42 at 32·5°; and H. Schiff represented it by the formula $(HO)_2=PO.O.Cr(OH)_2$. If the hexahydrate be left in contact with its mother-liquor, or with water, it forms a green, amorphous powder of the *tetrahydrate.* This change occurs if the crystals of the hexahydrate be left in contact with water, or with a soln. of sodium phosphate or of chrome-alum. The change is slow at low temp., for at 5° signs of the change appear only after 30 days, whereas at 100°, half an hour's boiling with water suffices for the production of the green, crystalline tetrahydrate. The violet crystals also passed into the green tetrahydrate when kept for 2 years at room temp. in air. The sp. gr. of the tetrahydrate is 2·10 at 32·5°. According to A. Carnot, the green hydrate is sparingly soluble in boiling water, and in soln. of ammonium nitrate, or acetate. C. L. Bloxam found it to be slowly dissolved by boiling conc. hydrochloric acid in sulphuric and hydrochloric acids, but the dihydrate is rather difficult to dissolve in the latter. C. L. Bloxam found that chromic phosphate is oxidized when boiled with nitric acid of sp. gr. 1·4 assisted by a little potassium chlorate. J. Dowling and W. Plunkett stated that the hydrated phosphate is not soluble in acetic acid, but is soluble in mineral acids from which it is precipitated unchanged by ammonia or ammonium sulphide. The hydrated phosphate is readily dissolved by alkali-lye, from which soln. it is deposited by boiling; but, added H. Kämmerer, much of the phosphoric acid remains in soln. A. F. Joseph and W. N. Rae said that chromite soln. are formed by the action of conc. alkali-lye, and that a soln. of sodium carbonate immediately converts the violet hexahydrate into a green basic salt, which retains alkali too tenaciously to be removed by washing. J. A. Hedvall observed that chromic phosphate reacts with barium oxide at 342°, forming barium phosphate and chromic oxide; and it reacts in an analogous manner with strontium oxide at 464°, and with calcium oxide at 517°.

S. M. Jörgensen prepared **chromic hexamminophosphate,** $[Cr(NH_3)_6]PO_4.4H_2O$, by adding sodium dihydrophosphate to a soln. of the hexamminotrinitrate, and then conc. ammonia. The yellow needles are sparingly soluble in water, and freely soluble in dil. acids, from which soln. the salt is precipitated unchanged by ammonia. It loses water slowly when confined in a desiccator over sulphuric acid; and rapidly when heated to 100° in air.

K. Haushofer obtained an acid salt—**chromic trihydrodiphosphate,** $CrH_3(PO_4)_2.8H_2O$—from a soln. of chromic phosphate in phosphoric acid; the triclinic crystals have the colour of chrome-alum, and are stable in air. A. Schwarzenberg obtained pale green hydrated **chromic pyrophosphate,** $Cr_4(P_2O_7)_3$, by adding sodium pyrophosphate to a soln. of chrome-alum; and L. Ouvrard, by melting sodium metaphosphate with chromic oxide. The pale green hydrate darkens at 100°, and loses nearly 3 mols. of water when heated. L. Ouvrard found that the monoclinic prisms obtained by his fusion process have a sp. gr. of 3·2 at 20°. The salt is soluble in soln. of sodium pyrophosphate, in strong mineral acids, in sulphurous acid, and in potash-lye. J. Persoz said that the pyrophosphate is not attacked by ammonium sulphide. A. Rosenheim and T. Triantaphyllides obtained salts of what they regarded as **chromipyrophosphoric acid,** $H(CrP_2O_7)$. Thus, by dropping into a sat. soln. of sodium pyrophosphate soln. a cold, conc. soln. of chromic chloride in conc. hydrochloric acid, grey **sodium chromipyrophosphate** is formed as an *octohydrate,* $Na(CrP_2O_7).8H_2O$, which becomes a pale green *pentahydrate* in a few days. Similarly, there were obtained pale green **potassium chromipyrophosphate,** $K(CrP_2O_7).5H_2O$; and grey, microscopic columns of **ammonium chromipyrophosphate,** $NH_4(CrP_2O_7).6H_2O$.

According to R. Maddrell, if a soln. of hydrated chromic oxide in an excess of dil. phosphoric acid be evaporated to dryness, and the product heated to 360°, **chromic metaphosphate,** $Cr(PO_3)_3$, is formed. K. R. Johnsson obtained it by heating chromic sulphate with metaphosphoric acid so as to drive off all the sulphuric acid; and P. Hautefeuille and J. Margottet, by melting chromic oxide or phosphate with four times its weight of metaphosphoric acid. The salt was prepared by J. Müller by treating 8 grms. of sodium metaphosphate with 300 c.c. of a conc. soln. of chrome-alum, with constant stirring at 70°; this soln. remains clear when boiled, or diluted with its own vol. of water. If this soln. be stirred for 4 days at ordinary temp. with 9 grms. of sodium metaphosphate, and the dark green solid be washed, and heated to 350°, chromic metaphosphate is produced. P. Hautefeuille and J. Margottet observed that the green, rhombic crystals are isomorphous with the metaphosphates of iron, aluminium, and uranium; K. R. Johnsson found the sp. gr. to be 2·974, and the mol. vol. 195. A. F. Joseph and W. N. Rae found that if heated for some time over a meker burner, it becomes brown, but regains its green colour on cooling; its sp. gr. is then 2·96, whilst the salt prepared by R. Maddrell's process had a sp. gr. of 2·93. The salt is insoluble in water and in mineral acids. P. Glühmann found that a violet crystalline or green amorphous **chromic triphosphate** is produced by the action of sodium triphosphate on a chromic salt—*vide* **8**. 50.

L. J. Cohen could not prepare **ammonium chromium phosphate,** by adding ammonium dihydrophosphate to a strongly acidic soln. of chromic chloride, but by reducing the acidity, a green, gelatinous precipitate with the composition $(NH_4)_2HPO_4.2CrPO_4.3H_2O$ was obtained; but if no hydrochloric acid or only a very small proportion was present **ammonium chromium hydroxyphosphate,** $5NH_4(H_2PO_4).2CrPO_4.4Cr(OH)_2$, was produced. L. J. Cohen found that the precipitate obtained on boiling soln. of chromic salts with sodium phosphate and acetic acid, is not, as C. L. Bloxam supposed, an impure chromic phosphate, but rather **sodium chromium phosphate,** $Na_2HPO_4.2CrPO_4.5H_2O$, which, when repeatedly washed with water, is converted into a basic salt. H. Grandeau obtained pale violet crystals of **potassium chromium phosphate,** $3K_2O.2Cr_2O_3.3P_2O_2$, by fusing a mixture of chromic and potassium phosphates.

K. A. Wallroth prepared **sodium chromium pyrophosphate,** $NaCrP_2O_7$, by cooling a molten mixture of microcosmic salt and chromic oxide; and L. Ouvrard obtained from a soln. of chromic oxide or chromic phosphate in molten sodium metaphosphate; or of chromic phosphate in molten sodium pyrophosphate. The green rhombic prisms have a sp. gr. 3·0 at 20°. S. M. Jörgensen treated a soln. of chromic hexamminonitrate with sodium pyrophosphate and then with ammonia. Yellow, six-sided plates of **sodium chromic hexamminopyrophosphate,** $Na[Cr(NH_3)_6]P_2O_7.11\frac{1}{2}H_2O$, were produced. The salt is insoluble in cold water; and when confined over sulphuric acid for a few months, it loses $10\frac{1}{2}$ mols. of water; at 130°, some ammonia as well as water is given off. J. Persoz treated a soln. of a chromic salt with potassium pyrophosphate, and obtained a soln. which was not precipitated by ammonium sulphide. L. Ouvrard melted potassium metaphosphate with chromic oxide, or potassium dichromate with chromic phosphate and obtained monoclinic prisms of **potassium chromic pyrophosphate,** $KCrP_2O_7$, of sp. gr. 3·5 at 20°.

C. Friedheim and I. Mozkin[3] prepared **ammonium phosphatotetrachromate,** $(NH_4O.CrO_2.O.CrO_2.O)_2 : PO.(ONH_4)$, by evaporating soln. of a mol each of ammonium dichromate and phosphorus pentoxide or from a soln. of equimolar proportions of ammonium dihydrophosphate and chromium trioxide, or by heating a mixture of 2 mols of phosphoric acid, 4 mols of chromium trioxide, 2 mols of ammonia, and a mol of ammonium dihydrophosphate. The salt forms dark red crystal aggregates; when the soln. of the salt is recrystallized from its aq. soln., ammonium dichromate, and phosphoric and chromic acids are formed. They also prepared **potassium phosphatodichromate,** $(KO.CrO_2.O.CrO_2.O)(KO) : PO.OH$, from a mixture of potassium dichromate with an excess of phosphoric acid. M. Blondel obtained it by mixing a highly conc. soln. of phosphoric and chromic acids, containing 8 mols of the latter to one mol of the former, with three-fourths of a mol of potassium carbonate. A salt of the composition $3K_2O.P_2O_5.8CrO_3$, or **potassium phosphatotetrachromate,** $(KO.CrO_2.O.CrO_2.O)_2PO(OK)_2$, is precipitated in the form of small, short prisms. If the soln. contains only two mols of chromic acid, needles of the phosphatodichromate are formed. If the latter soln., however, is mixed with some crystals of the first salt, the precipitate at first consists of phosphatotetrachromate, but, if left in contact with the liquid, it is converted into the phosphatodichromate. The phosphatotetrachromate is converted into the phosphatodichromate by treatment with water or with a sat. soln. of potassium dichromate. For some complex phosphohalides, *vide supra*, chromyl chloride.

REFERENCES.

[1] A. Moberg, *Journ. prakt. Chem.*, (1), **44**. 328, 1848 ; H. Moissan, *Ann. Chim. Phys.*, (5), **25**. 415, 1882 ; C. U. Shepard, *Contributions to Mineralogy*, New York, 1877 ; *Bull. Soc. Min.*, **1**. 140, 1878 ; A. Colani, *Compt. Rend.*, **158**. 794, 1914.

[2] J. Dowling and W. Plunkett, *Chem. Gaz.*, **16**. 220, 1858 ; R. Maddrell, *Mem. Chem. Soc.*, **3**. 273, 1846 ; *Phil. Mag.*, (3), **30**. 322, 1847 ; W. Lapraik, *Journ. prakt. Chem.*, (2), **47**. 305, 1893 ; S. M. Jörgensen, (2), **30**. 26, 1884 ; C. F. Rammelsberg, *Pogg. Ann.*, **68**. 383, 1846 ; H. Rose, *ib.*, **83**. 143, 1851 ; G. Köthe, *Dingler's Journ.*, **214**. 59, 1874 ; J. A. Hedvall and J. Heuberger, *Zeit. anorg. Chem.*, **135**. 49, 1924 ; H. Schiff, *ib.*, **43**. 304, 1904 ; *Gazz. Chim. Ital.*, **35**. i, 368, 1905 ; J. Arnaudon, *Le Technologiste*, **21**. 522, 1859 ; E. Mathieu-Plessy, *Répert. Chim. Appl.*, **4**. 453, 1862 ; A. Étard, *Compt. Rend.*, **84**. 1091, 1877 ; P. Hautefeuille and J. Margottet, *ib.*, **96**. 849, 1883 ; A. Carnot, *ib.*, **96**. 1313, 1882 ; *Bull. Soc. Chim.*, (2), **37**. 482, 1882 ; W. J. Sell, *Proc. Cambridge Phil. Soc.*, **12**. 388, 1904 ; C. L. Bloxam, *Chem. News*, **52**. 194, 1885 ; A. F. Joseph and W. N. Rae, *Journ. Chem. Soc.*, **111**. 196, 1917 ; H. T. S. Britton, *ib.*, 614, 1927 ; H. Kämmerer, *Zeit. anal. Chem.*, **12**. 375, 1873 ; L. Ouvrard, *Recherches sur l'action des phosphates alcalins sur quelques oxydes metalliques*, Paris, 1888 ; *Ann. Chim. Phys.*, (6), **16**. 344, 1889 ; H. Grandeau, *De l'action du sulfate de potasse à température élevée sur les phosphates métalliques*, Paris, 1886 ; *Ann. Chim. Phys.*, (6), **8**. 222, 1886 ; L. N. Vauquelin, *ib.*, (1), **25**. 21, 194, 1798 ; (1), **70**. 70, 1809 ; J. Persoz, *ib.*, (3), **20**. 315, 1847 ; K. R. Johnsson, *Ber.*, **22**. 976, 1889 ; K. A. Wallroth, *ib.*, **16**. 3059, 1883 ; *Oefvers. Akad. Forh.*, 40, 1883 ; *Bull. Soc. Chim.*, (2), **39**. 316, 1883 ; J. Müller, *Beiträge zur Kenntnis der Metaphosphate*, Berlin, 26, 1906 ; P. Glühmann, *Beitrag zur Kenntnis der Triphosphorsäure und ihrer Salze*, Berlin, 43, 1899 ; A. Schwarzenberg, *Untersuchungen über die pyrophosphorsauren Salze*, Göttingen, 1849 ; *Liebig's Ann.*, **65**. 149, 1848 ; W. Muthmann and H. Heramhof, *ib.*, **355**. 154, 1907 ; G. Schnitzer, *Deut. Industrie Ztg.*, 29, 1862 ; *Viertelj. tech. Chem.*, **4**. 1, 1862 ; K. Haushofer, *Zeit. Kryst.*, **7**. 263, 1883 ; J. Dingler, *Wagner's Jahresber*, 405, 1873 ; L. J. Cohen, *Journ. Amer. Chem. Soc.*, **29**. 1194, 1907 ; N. R. Dhar, K. C. Sen and N. G. Chatterji, *Koll. Zeit.*, **33**. 29, 1923 ; A. Rosenheim and T. Triantaphyllides, *Ber.*, **48**. 582, 1915 ; J. A. Hedvall, *Zeit. Elektrochem.*, **36**. 853, 1930.

[3] I. Mozkin, *Ueber Kondensationsproducte von Phosphaten, Arsenaten oder Nitraten der Alkalien mit Chromaten oder Sulfaten derselben*, Berlin, 1894 ; C. Friedheim and I. Mozkin, *Zeit. anorg. Chem.*, **6**. 284, 1894 ; M. Blondel, *Compt. Rend.*, **118**. 194, 1894.

CHAPTER LXI

MOLYBDENUM

§ 1. History of Molybdenum

The extraordinary confusion in the use of the terms plumbago, graphite, galena, and molybdena, which prevailed from the time of Aristotle, *circa* 350 B.C. to the 18th century, has been discussed in connection with carbon, and with galena. It is very difficult to pick out from the various references those which in all probability refer to molybdena. The term *molybdœna* is the Latinized form of the Greek *μολύβδαινα*, which is derived from *μόλυβδος*, lead. The term *μολύβδαινα* appears to have been applied by Aristotle,[1] Dioscorides, Galen, Pliny, etc., to various things associated with lead—plummets, sinkers for fishing nets, bullets for catapults, etc.—to lead oxide obtained as a by-product in cupellation, and to natural lead ores.

According to J. W. Evans, during the 17th century, the terms *lapis plumbarius*, *plumbago*, and *galena*, and exceptionally *molybdœna*, were employed in the sense of graphite, including, probably, molybdenite with which it was confounded. Later, molybdæna was commonly employed for graphite, and galena became identified with the mineral which now bears that name. It was soon recognized that molybdæna and graphite did not contain lead; and those who experimented on molybdæna seem to have regarded it as a kind of zinc sulphide. J. F. Henckel,[2] for instance, used the molybdæna for zinc-blende; and J. G. Hoffmann and J. B. Böhmer associated the term molybdæna with tin, and they also confused it with graphite. In his work on *nihil* or sublimed zinc oxide, I. Lawson described molybdæna, and this appears to have been molybdenite, although he believed it to be identical with graphite. J. G. Wallerius' minerals *ren Blyertz* or molybdæna pura, and *oren Blyertz* or molybdæna impura included graphite and molybdenite. In 1754, in a paper: *Rön om Blyerts*—the Swedish term for graphite, B. Qvist described some experiments on a mineral occurring in flexible plates which must have been molybdenite. A. von Cronstedt's description of *molybdena membranacea nitens* from Bispberg, Sweden, is applied to the molybdenite employed in B. Qvist's experiments. J. W. Baumer distinguished the non-combustible Wasserbley or molybdæna of Bispberg from the combustible Wasserbley or molybdæna or *plumbum scriptorum* used for making pencils. C. Linnæus referred to *molybdœnum tritura cœrulescente*, or molybdenum with a bluish streak; and this was possibly the mineral investigated by B. Qvist.

The confused ideas which prevailed up to 1778 as to the nature of graphite and molybdenite were at length dissipated by the work of C. W. Scheele described in papers entitled *Försök med Blyerts, Molybdœna* (1778), and *Försök med Blyerts, Plumbago* (1779). In his first paper, C. W. Scheele showed that the *molybdœna membranacea nitens* on which B. Qvist made his experiments, is a combination of an acid of a metallic nature with sulphur; and in his second paper, he demonstrated that the *molybdenœna textura micacea et granulata* of A. von Cronstedt, is a mineral charcoal composed of an aerial acid—carbonic acid—and phlogiston with a small proportion of pyrites. Translating C. W. Scheele's statement into modern nomenclature: aerial acid+phlogiston=carbon. It is not stated why the term molybdæna was allocated to molybdenite when, at that period, graphite was the more usual term; but afterwards, when he wanted a term for graphite, he naturally adopted the Latin term plumbago. C. W. Scheele's usage fixed the subsequent terms molybdæna and graphite or plumbago. For example, T. Bergman, W. Withering, J. Fibig, A. G. Werner, D. L. G. Karsten, and R. Kirwan followed C. W. Scheele. J. B. L. Romé de l'Isle was studying graphite at the same time as C. W. Scheele, and he expressed the belief that C. W. Scheele's molybdæna is micaceous iron ore, *mine de fer micacée grise,* and that his plumbago owed its action on nitre *au fer noirâtre phlogistiqué, en un mot à l'éthiops martial natif et à la matière grasse qui s'y rencontrent.* The subject was discussed by B. G. Sage, and P. J. Macquer.

In 1782, P. J. Hjelm[3] separated the metal from molybdæna, and called it **molybdenum.** B. Pelletier also isolated the metal which was thereafter studied by J. J. Berzelius, and C. F. Bucholz. R. Kirwan[4] applied the term **molybdenite** to the metal, but A. Brongniart's use of the term molybdenite for the mineral sulphide is in general use in England and France. In Germany, the old term *Molybdän,* as well as D. L. G. Karsten's term *Molybdänglanz,* are used for the sulphide.

M. Ogawa[5] reported that molybdenite and thorianite contain a new element closely allied to molybdenum, and probably identical with the new tin-group element reported by C. de B. Evans in thorianite. The element was said to differ from molybdenum in being soluble in hot conc. hydrochloric acid, and in giving no colour reaction when its higher oxide is reduced with tin and hydrochloric acid either in the presence or absence of potassium thiocyanate. M. Ogawa also reported another element which he called *nipponium,* to occur in molybdenite, thorianite, and reinite; this element was said to fill the gap between molybdenum and ruthenium. These results have not been confirmed. R. Nasini and E. Baschieri could find no nipponium in the molybdenite from Stilo, Calabria. G. G. Boucher[6] extracted from cast-iron and blast-furnace boiler-dust "a new element" which was shown by F. G. Ruddock, and C. H. Jones to be molybdenum mixed with iron.

M. Gerber reported that molybdenum is not a simple substance, but that it is accompanied by an isotope which is chemically and spectroscopically identical. He called this element *neomolybdenum.* He said that neomolybdenum was separated from molybdenum by fractional crystallization of a specimen of ammonium molybdate prepared from molybdenite from Glen Innis, New South Wales. The most soluble fractions, when analyzed, have for the metal an at. wt.$=99{\cdot}9$ (Mo$=96$), and, moreover, the acidic oxide obtained by heating this ammonium salt was far more volatile than ordinary molybdic acid. These statements have not been confirmed.

REFERENCES.

[1] Aristotle, *De generatione animalium,* **2.** 2; Dioscorides, *Materia medica,* **5.** 100; Galen, *De simplicium medicamentorum temperamentis,* **9.** 3, 22; *De compositione medicamentorum per genera,* **1.** 11; Pliny, *Historia naturalis,* **33.** 31, 35; **25.** 97; **29.** 26; **33.** 31, 35; **34.** 50, 53; **37.** 18; J. W. Evans, *The Meanings and Synonyms of Plumbago,* Hertford, 1908.

[2] J. F. Henckel, *Acta physico-medica naturæ curiosorum,* Nurimbergæ, **4.** 308, 1737; J. G. Hoffmann and J. B. Böhmer, *De matricibus metallorum,* Leipzig, 1738; I. Lawson, *Dissertatio sistens nihil,* Leyden, 1737; J. G. Wallerius, *Mineralogia,* Stockholm, 1747; B. Qvist, *Svenska Akad. Handl.,* **15.** 189, 1754; C. W. Scheele, *ib.,* **39.** 247, 1778; **40.** 238, 1779; A. von Cronstedt, *Försök til Mineralogie,* Stockholm, 1758; J. W. Baumer, *Naturgeschichte des Mineralreichs,* Gotha, **1.** 151, 217, 1763; **2.** 105, 139, 1763; C. Linnæus, *Systema naturæ,* Stockholm, 128, 1768; T. Bergman, *Sciagraphia,* Leipzig, 93, 1782; W. Withering's translation, London, 64, 1783; R. Kirwan, *Elements of Mineralogy,* London, 357, 1784; J. Fibig, *Handbuch der Mineralogie,* Mainz, 52, 273, 1787; A. G. Werner, *Berg. Journ.,* 393, 1789; D. L. G. Karsten, *Museum leskeanum regnum minerale,* Leipzig, **2.** i, 337, 1789; J. B. L. Romé de l'Isle, *Cristallographie,* Paris, **2.** 501, 1783; *Description méthodique d'une collection de minéraux de M.D.R.D.L.,* Paris, 165, 1773; B. G. Sage, *Élémens de minéralogie docimastique,* Paris, **1.** 194, 1777; **2.** 501, 1777; P. J. Macquer, *Dictionnaire de chimie,* Paris, 1778.

[3] P. J. Hjelm, *Svenska Akad. Nya Hand.,* **9.** 288, 1788; *Crell's Ann.,* i, 391, 1790; i, 179, 248, 266, 353, 429, 1791; ii, 59, 1791; i, 260, 1792; ii, 358, 1792; i, 238, 1794; B. Pelletier, *Obs. Phys.,* **27.** 343, 434, 1785; J. J. Berzelius, *Svenska Akad. Handl.,* 145, 1825; *Pogg. Ann.,* **4.** 153, 1825; **6.** 331, 369, 1826; **7.** 261, 1826; *Ann. Chim. Phys.,* (2), **17.** 5, 1821; *Schweigger's Journ.,* **22.** 51, 1817; **47.** 87, 1826; *Ann. Phil.,* **11.** 235, 1826; *Edin. Journ. Science,* **4.** 133, 1826; C. F. Bucholz, *Scherer's Journ.,* **9.** 485, 1803; *Gehlen's Journ.,* **4.** 598, 1803; *Phil. Mag.,* **16.** 193, 1803; *Nicholson's Journ.,* **20.** 121, 188, 253, 1808; *Journ. Mines,* **18.** 241, 1808.

[4] R. Kirwan, *Elements of Mineralogy,* Dublin, **2.** 58, 1796; A. Brongniart, *Traité élémentaire de minéralogie,* Paris, **2.** 92, 1807; D. L. G. Karsten, *Mineralogische Tabellen,* Berlin, 70, 1808.

[5] M. Ogawa, *Chem. News,* **98.** 261, 1908; *Journ. Coll. Science Tokyo,* **25.** 15, 16, 1908;

R. Nasini and E. Baschieri, *Atti Accad. Lincei*, (5), **21**. 692, 1912; C. de B. Evans, *Journ. Chem. Soc.*, **93**. 666, 1908.

[6] G. G. Boucher, *Chem. News*, **76**. 99, 1897; F. G. Ruddock, *ib.*, **76**. 118, 1897; C. H. Jones, *ib.*, **76**. 171, 1897; M. Gerber, *Monit. Scient.*, (5), **7**. 73, 121, 169, 219, 1917.

§ 2. The Occurrence of Molybdenum

Molybdenum does not occur in the elemental form in nature. Its compounds are among the scarcer constituents of the earth's crust. According to F. W. Clarke and H. S. Washington,[1] the average proportion of molybdenum in the igneous rocks of the earth's crust is $n \times 10^{-6}$ per cent. J. H. L. Vogt estimated $n \times 10^{-7}$ per cent. W. Vernadsky gave $0{\cdot}0_5 9$ for the percentage amount, and $0{\cdot}0_4 5$ for the atomic proportion. W. and J. Noddack and O. Berg gave 10^{-7} for the absolute abundance of molybdenum on the earth. The general subject was discussed by H. S. Washington, G. Tammann, V. M. Goldschmidt, E. Herlinger, A. von Antropoff, O. Hahn, and J. Joly. H. A. Rowland [2] included molybdenum among the elements which had been detected spectroscopically in the sun; although C. C. Hutchins and E. S. Holden failed to detect molybdenum lines in the solar spectrum. J. N. Lockyer, however, attributed certain lines in the spectrum of the sun to molybdenum; and S. Albrecht detected the lines of this element in the spectrum of γ-Geminorum.

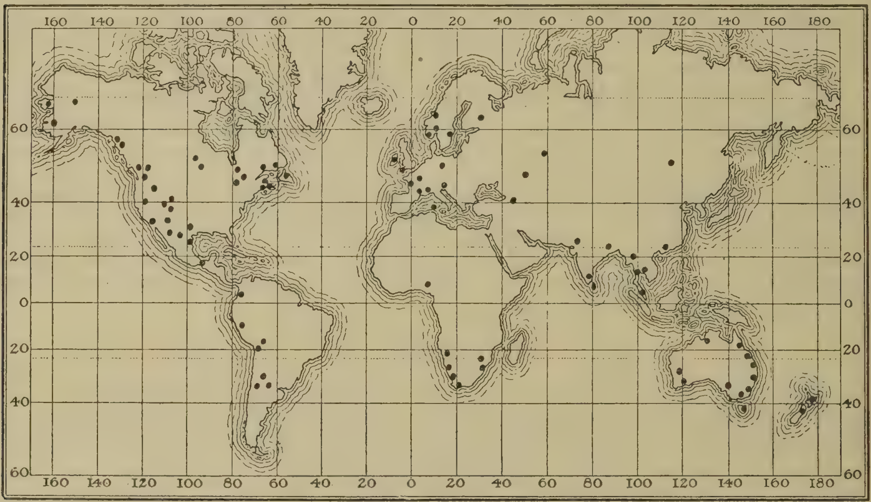


FIG. 1.—Geographical Distribution of the Molybdenum Ores.

The two minerals of practical importance are molybdenite, MoS_2, and wulfenite, $PbMoO_4$. Molybdenite—molybdenum sulphide—is a pneumatolytic product derived from granitic magmas. Most of the occurrences of molybdenite are closely associated with acidic plutonic rocks, particularly the granites. It occurs embedded in the granite itself, or along open joints or in dykes cutting the granite or the neighbouring rocks. It also occurs in deep-seated veins allied to the pegmatites, or in the fissure veins of metalliferous lodes. The mineral is here of direct magmatic origin, and is concentrated in the later solidifying portions of the magma along with tin, wolfram, and sulphides; and it is frequently associated with fluoriferous minerals—tourmaline, topaz, and fluorspar. Molybdenite is sometimes associated with crystalline limestone or lime-silicate rocks formed by the thermal metamorphism and metasomatism of calcareous deposits near the granite. This case is illustrated by some of the Canadian deposits where the molybdenite has been produced by the transfer of material from the granitic magma to the sediment, and recrystallization. In the west of the United States, the wulfenite—lead molybdate—is usually a secondary mineral which has been formed in the oxidation zone of the upper levels for both lead and molybdenum occurs as sulphides lower down. The subject was discussed by G. O. Smith,[3] A. R. Crook, J. W. Wells, W. H. Emmons, W. C. Brögger, F. Schafarzik, R. Brauns, L. W. Staples and C. W. Cook, and E. Thomson.

The geographical distribution[4] of the more important molybdenum ores is summarized in the map, Fig. 1. The chief localities are as follow:

Europe.—Small quantities of molybdenite have been reported from a number of localities in the **British Isles**[5]—*e.g.*, at Lalant, Marazion, St. Day, Guinear, etc. in Cornwall; Mount Sorrel, Leicestershire; Carrock Fell, Cumberland; Tomnadashan, Perthshire; in the granites of Galloway, Argyleshire, and Inverness; Murvey, Galway; near Lough Laragh, Inishdovey, Donegal. In no case is any deposit of commercial value. No deposits are worked in **France**[6] on a commercial scale. Molybdenite has been reported at Miséri, near Nantes; in Haute Vienne; at St. Léonard, Limoges; Chessy, in the Central Plateau; the red granite of Glacier de la Meije, Dauphiné; in the gneiss near the Mer de Glace; and in the Vosges. Molybdenum concentrates have been exported from **Spain.**[7] There are molybdenum occurrences on the Sierra de Guadarrama, Villacastin, Navacerrada, Hoyo de Manzanares, and at the Torrelodones tunnel; also at Cuevas de Salabe, Asturias; Espinabel, Gerona; Socorro mine, Linares; Madronal, San Roque, Sierra de Mijas, Málaga; Sierra Nevada and in several places in Granada. It also occurs at Vélez de Benaudella, and Güéjar, Sierra, near Albunuelas; in the Umbrua del Madronal; and in Almeria. Molybdenite occurs in a few places in **Italy**[8]—*e.g.* Traversella, Drusacco, Quittengo, Bolladore, Villaputzu, Sardinia, and at Monte Somma. In **Switzerland,**[9] occurrences of molybdenum have been observed at Binnenthal, Lucendro, Mürtschenalp, Aletsch, and Visp; and in **Austria,**[10] at Salzberg, Zillerthal, and Schmirn. Occurrences have been found in **Yugo-Slavia**[11]—*e.g.* in Carinthia (Slovenia). Molybdenite occurs in various parts of **Russia**[12]—*e.g.* near Bash Abaran, Caucasus; in the Zanguezar district, on the Ilmensky Hills, near the River Cherelipanky; there are deposits in **Finland,**[13] and at Mätäsvaara, and Pitkäranta. In **Germany,**[14] molybdenite occurs as a rare constituent of the stanniferous veins of Geyer, Erzgebirge; at Sanberge, Ehrenfriedersdorf; and at Sadisdorf, Saxony. Molybdenite occurs in **Sweden**[15] near Nörrköping; and on the Island of Ekholmen in Vestervik. There are important deposits of molybdenum ore in **Norway,**[16] which is regarded as one of the principal producers. Most of the Norwegian output is from mines in the districts of Knaben, Moi, Siredalen, Mandal, Telemarken, Drammen, and Haugesund. The ore has been worked on a small scale at Syversvolden, Ostvaago, Smölen, Langvaten, and Tjaardalskampen. Molybdenite is an accessory constituent of many of the igneous rocks of Norway—Laurvik, Frederiksvärn, Langesundfjord, Lövö, and Klokkerholmen.

Asia.—A. E. Fersman[17] reported molybdenite in the Selengan Dauria, **Transbaikalia.** Molybdenite occurs in a vein of pegmatite at Hetimulla, Kegalla, and Saffragam in **Ceylon.**[18] Considerable amounts of molybdenite are associated with wolfram and tin in **Burma**[19]—*e.g.* Yamethin, South Shan States, Thaton, Tavoy, and Mergui. In **India,**[20] molybdenite occurs in the rocks of Chota Nagpur; Rajputana; South Travancore; Madura; Trichinopoly; Kurinavaram; Mangamalai; Oregum, Mysore; Patria River, Mahabagh; and Urmi, Bengal. Molybdenum ores have been reported at Chantabun on the east coast of **Siam**;[21] in Kwang-tung in **China**; and at Gifu, Toyania, Niigata, Totori, and Hyogo in **Japan.**[22] In **Siberia,**[23] and Asiatic Russia, there are deposits in the Kirghiz Steppes, and in the Transbaikul province, etc.

Africa.—J. Barthoux[24] described the deposits of wulfenite in **Morocco**; G. Castelli, those in Portuguese **Angoli**; and R. A. Farquherson, those in **Somaliland.** Molybdenite has been reported in Nigeria[25] near Jos, and in the Jarawa Hills, as well as in the cassiterite veins of Dogon Daji. In **Southern Rhodesia,**[26] molybdenite occurs at Umtali, Hartley district, and near Bulawayo; in **South West Africa,**[27] south of Usakos; in the Kuiseb Valley; at Aus, and in the Velloor Hills, Warmbad district; at Gansberg; and Tsumeb. The ore occurs in many places in the **Union of South Africa**[28]—*e.g.* in the granite rocks near Stellenbosch, Cape Province; in various localities of the copper district of Little Namaqualand; in the Transvaal at Appingadam, Stavoreu, Enkeldoorn, and Houlenbek; and in Natal in the valley of Hlatimba, and at Umkukuse, Subeni, and in Buffalo valley.

North America.—Extensive deposits of molybdenite occur in **Canada**[29]—British Columbia, Manitoba, New Brunswick, Nova Scotia, Ontario, Quebec, and Newfoundland. Deposits occur in the **United States**[30] in Arizona, California, Colorado, South Dakota, Maine, Montana, Nevada, New Mexico, Texas, Utah, and Washington. Molybdenite occurs in Shaken in **Alaska.**[31] Molybdenite has been reported from the Leeward Islands, **West Indies**;[32] and from Hawaii.[33] Ores have been reported from a dozen states in **Mexico**[34]—San José, Tamaulipas; Nacosari, Sonora; Sahuaripa, El Poovenir, Temascaltepec, Chihuahua, Hidalgo, etc. Molybdenite also occurs in Central America.[35]

South America.—Molybdenite has been found in **Argentina,**[36] at San Virgilio, Sierra de Cordoba; and Los Coloraditos, Sierra de Velasco. In **Bolivia,**[37] the mineral occurs in the Tasna district, Oruro; and in Larecaja, La Paz. In **Chile,**[38] molybdenite has been reported at Cupane, and La Punta. In **Peru,**[39] in the Jauja province, Junin; at Runatullo, Picran; Torrioc ridge, Janchis-Jucha; Tipillapa; and Caseas, Contumaza. In **Brazil,**[40] at Vallongo. It also occurs at Santa Rita and Patagonia.[41]

Australasia.—In **New South Wales,**[42] molybdenite occurs in the New England district—Wilson's Downfall, Rock River or Wanglebung, Bolivia, Deepwater, Glen Eden, Kingsgate, Yarrow Creek, Booralong or Balderleigh, Attunga and Moonbi; in the Yetholme district—Mount Tennyson, Gemaila, and Tarana; and in the Whipstick district—Jingera, Mount Metallic, Black Range, and Tantawanglo. In the **Northern Territory,**[43] deposits occur at Yenberrie, and Hatches Creek. In **Queensland,**[44] there are large deposits of molybdenum ore, at Stanthorpe, Ballandean; in the northern area in the Chillagoe district; the Wolfram area, the Bamford Mining field; Rocky Creek area; Khartoum area; Tyrconnel; Mt. Perry; and Boomarrie. In **South Australia,**[45] molybdenum occurs in the Moonta and Walaroo areas. In **Victoria,**[46] molybdenum ore occurs at Wangrabelle, Gippslund; and at Everton, in the Beechworth district. In **West Australia,**[47] molybdenum ores occur near the Yalgoo goldfield; near Leonora; at Callie Soak; Coolgardie; in the Mount Margaret goldfield; at Southern Cross, Swan View, Wagin, Ravensthorpe, Clackline, and Blackboy Hill. In **New South Wales,**[48] mobybdenite occurs near Kingsgate. In **Tasmania,**[49] small deposits occur in various localities—*e.g.* on the West side of Mt. Stronach; in the hinterland of Scamander district; in the district of Moina; East of River Forth; King Island; and South Heemshirk. In **New Zealand,**[50] molybdenite has been reported at Ohio Creek, Thames Goldfield; at Fourteen-mile Creek, Greymouth; in the Mt. Radiant district; near Specimen Creek; at Richmond Hill, Parapara; Bravo Island; and near Dusky Sound.

Before 1914, molybdenum metal sold at about 6/– per lb.; in 1918, ferromolybdenum with 50 to 60 per cent. molybdenum sold at about 16/– per lb.; and in 1920, at about 9/6 per lb. The price of molybdenum ore in 1924 ranged from 52*s.* 6*d.* to 55*s.* 0*d.* per unit. Reliable data for estimating the world's output have been available only in comparatively recent times. Until the demand for molybdenum for the manufacture of special steels arose, the greater part of the world's output was absorbed in the manufacture of a few chemical reagents. R. H. Rastall[51] estimated for 1915–1920 the proportion of metal in metric tons contained in the concentrates produced by different countries, to be as follows:

	1915	1917	1918	1920
Australia . . .	70·8	94·4	105·1	35·5
Bolivia . . .	6·5	—	—	—
Canada . . .	8·0	89·9	102·9	nil
Chile . . .	—	20·1	—	—
China . . .	—	2·4	1·1	—
Korea . . .	—	59·2	10·7	—
Japan . . .	—	12·1	70·3	—
Mexico . . .	—	—	14·0	0·3
Norway . . .	72·3	82·1	84·9	—
Peru . . .	1·3	3·8	1·3	1·0
Spain . . .	5·2	—	—	—
Sweden . . .	—	20·3	25·1	—
United States . .	82·4	158·8	390·8	15·8

The minerals containing molybdenum include the crystalline sulphide, **molybdenite,** MoS_2, or the colloidal form, **jordisite:** the molybdates, **wulfenite,** $PbMoO_4$; **powellite,** $CaMoO_4$, associated with $CaWO_4$; **belonosite,** $MgMoO_4$; **molybdic ochre,** or **molybdite,** $MoO_3.nH_2O$, and $Fe_2(MoO_4)_3.nH_2O$—possibly a mixture; **ochrematite,** $3\{3Pb(AsO_4)_2.PbCl_2\}.4Pb_2MoO_5$; **ferrous tetramolybdite** of M. Spica;[52] **pateraite,** impure $CoMoO_4$; **ilsemannite,** or blue oxide, $MoO_2.4MoO_3$, or $Mo_3O_8.nH_2O$.

W. F. Hillebrand[53] reported on the molybdenum content of the American rocks; and M. Spica analyzed the molybdenum minerals of Stilo, Calabria. C. J. Heine discussed the molybdenum content of the copper *schists* of Mansfield, and P. Krusch, that of Rickelsdorf; K. Chuboda, that of *manganese diaspore;* C. D. Braun, that of the vanadiferous *iron ores of* Xaverloh, Harz; F. Wöhler, that of *iron*, and *iron slags;* L. A. Palmer, *clays;* C. R. Fresenius and E. Hintz, that of *hardhead tin;* H. Traube, that of *scheelite;* H. St. C. Deville, that of *rutile;* C. de B. Evans, that of *thorianite*, and W. Steinkuhler, that of *pitchblende;* A. Jorissen discussed the occurrence of molybdenum in the Liège coal-field; and H. Ramage, in the flue-dusts from South

Yorkshire coals. A. Schacci observed that a small proportion of molybdenum occurs in the crusts of the fumaroles in the craters of Vesuvius; J. B. Ferguson, in the volcanic lava of Hawaii; and F. Zambonini, in vesbine in crevices of the Vesuvian lava of 1631. T. L. Phipson showed that the so-called vesbium (**9**. 53, 1) is a mixture of copper and molybdenum.

E. Demarçay [54] observed molybdenum occurring in the ashes of some plants—Scotch fir, silver fir, vine, oak, poplar, and hornbeam; and F. von Oefele, in the excrement of animals.

References.

[1] F. W. Clarke and H. S. Washington, *Proc. Nat. Acad.*, **8**. 112, 1922; *The Composition of the Earth's Crust*, Washington, 21, 1924; H. S. Washington, *Trans. Amer. Inst. Min. Eng.*, **39**. 735, 1908; *Proc. Nat. Acad.*, **1**. 574, 1915; *Journ. Franklin Inst.*, **190**. 777, 1920; *Bull. Soc. Nat. Research Council*, **2**. ii, 30, 1926; *Journ. Washington Acad.*, **14**. 435, 1924; *Amer. Journ. Sciences* (4), **38**. 90, 1914; (5), **9**. 351, 1925; (5), **12**. 272, 1926; V. M. Goldschmidt, *Videnskapssilskapet, Schrift.*, 11, 1922; 3, 1923; *Zeit. Elektrochem.*, **28**. 411, 1922; *Der Stoffwechsel der Erde*, Kristiania, 1922; G. Tammann, *Zeit. anorg. Chem.*, **131**. 96, 1923; **134**. 269, 1924; E. Herlinger, *Fortschr. Min.*, **12**. 253, 1927; A. von Antropoff, *Sitzber. Nat. Hist. Ver. Rheinlande*, 1, 1926; O. Hahn, *Naturwiss.*, **14**. 159, 1926; W. and J. Noddack and O. Berg, *ib.*, **13**. 568, 1925; J. Joly, *The Surface History of the Earth*, Oxford, 1925; J. H. L. Vogt, *Zeit. prakt. Geol.*, **6**. 226, 315, 1898; **7**. 10, 274, 1899; **14**. 223, 1906; W. Vernadsky, *Essai de minéralogie descriptive*, St. Petersburg, **1**. 121, 740, 1914; *La geochimie*, Paris, 16, 1924; A. E. Fersman, *Bull. Acad. St. Petersburg*, (6), **6**. 367, 1912.

[2] H. A. Rowland, *Johns Hopkins Univ. Circular*, 85, 1891; *Chem. News*, **63**. 133, 1891; *Amer. Journ. Science*, (3), **41**. 243, 1891; C. C. Hutchins and E. S. Holden, *ib.*, (3), **34**. 451, 1887; *Phil. Mag.*, (5), **24**. 325, 1887; J. N. Lockyer, *Phil. Trans.*, **172**. 561, 1881; *Proc. Roy. Soc.*, **27**. 279, 1878; S. Albrecht, *Astrophys. Journ.*, **72**. 65, 1930.

[3] G. O. Smith, *Bull. U.S. Geol. Sur.*, 260, 1905; W. H. Emmons, *ib.*, 432, 1910; A. R. Crook, *Bull. Amer. Geol. Soc.*, **15**. 283, 1904; J. W. Wells, *Canadian Min. Rev.*, **22**. 113, 1903; R. Brauns, *Centr. Min.*, 97, 1908; W. C. Brögger, *Zeit. Kryst.*, **16**. 158, 1890; F. Schafarzik, *Földt. Közl.*, **38**. 657, 1908; E. Thomson, *Econ. Geol.*, **13**. 302, **1918**.

[4] B. Simmerbach, *Zeit. prakt. Geol.*, **28**. 47, 59, 1920; A. H. Hunter, *Yearbook Amer. Iron Steel Inst.*, **11**. 127, 1921; J. P. Bonardi, *Chem. Met. Engg.*, **21**. 364, 1919; **23**. 205, 1920; S. J. Johnston, *Journ. Soc. Chem. Ind.*, **37**. 448, R, 1918; H. Fleck, *Iron Age*, **98**. 1117, 1916; A. N. Winchell, *Econ. Geol.*, **5**. 158, 1910; *Mining World*, **33**. 17, 1910; J. D. Cutter, *Eng. Min. Journ.*, **121**. 90, 1926; L. W. Staples and C. W. Cook, *Amer. Min.*, **16**. 1, 1931; C. Baskerville, *Eng. Min. Journ.*, **86**. 1055, 1908; J. W. Wells, *Journ. Canada Mining Inst.*, **6**. 47, 1903; A. Haenig, *Oesterr. Zeit. Berg. Hütt.*, **56**. 177, 1908.

[5] C. le Neve Foster, *Min. Mag.*, **1**. 74, 1877; *Geol. Mag.*, (1), **3**. 526, 1866; A. M. Finlayson, *ib.*, (5), **7**. 19, 1910; A. Harker and J. E. Marr, *Journ. Geol. Soc.*, **47**. 266, 1891; M. F. Heddle, *The Mineralogy of Scotland*, Edinburgh, **1**. 15, 1901; A. Russell, *Min. Mag.*, **19**. 19, 1920; H. M. Cadell and J. C. G. Wilson, *Proc. Roy. Phys. Soc. Edin.*, **8**. 204, 1884; G. H. Kinahan, *Trans. Inst. Min. Eng.*, **26**. 265, 1904; *Journ. Geol. Soc. Ireland*, **8**. 55, 1904; R. P. Greg and W. G. Lettsom, *Manual of the Mineralogy of Great Britain and Ireland*, London, 349, 1858; A. Strahan, J. S. Flett, and C. H. Dinham, *Special Reports on the Mineral Resources of Great Britain*, London, **5**. 28, 1916; H. Dewey, *ib.*, **1**. 23, 30, 1916.

[6] R. H. Rastall, *Geol. Mag.*, (6), **5**. 196, 1918; F. J. Stephens, *Trans. Inst. Min. Met.*, **27**. 198, 1918; A. Lacroix, *Minéralogie de la France et de ses colonies*, Paris, **2**. 463, 1897.

[7] D. L. Mallada, *Explicacion del mapa geologico de Espana*, **1**. 177, 1895; *Mapa Geologico de Espana*, Madrid, 1919; J. M. Rubio and J. Gavala, *Bol. Inst. Geol. Espana*, (2), **19**. 165, 1918; C. F. A. Tenne and S. Calderon, *Die Mineralfundstätten der Iberischen Halbinsel*, Berlin, 62, 1902; Anon., *Min. Journ.*, **119**. 718, 1917; L. F. Navarro, *Soc. Espan. Hist. Nat.*, **3**. 3, 1894.

[8] R. Nasini and E. Baschiere, *Atti Accad. Lincei*, (5), **21**. i, 692, 1912; T. Sotgiu, *Rass. Min.*, **55**. 33, 1921; A. Martelli, *ib.*, **54**. 99, 1921; E. Repossi, *Atti Accad. Lincei*, (5), **32**. 57, 1923; A. d'Achiardi, *Mineralogia della Toscana*, Pisa, **2**. 328, 1873; W. P. Jervis, *Il tesori sotterranei dell'Italia*, Turin, **1**. 84, 123, 126, 133, 219, 1873; **3**. 36, 180, 1881; G. Lincio, *Centr. Min.*, 12, 1905; G. vom Rath, *Sitzber. Niederrh. Ges. Bonn*, 67, 1886; O. Silvestri, *Neues Jahrb. Min.*, i, 434, 1894; G. Guili, *Saggio di statisca mineralogica della Tosca*, Bologna, 1843; *Nuovi Ann. Scien. Nat.*, **8**. 5, 401, 1842; **9**. 160, 385, 1843; **10**. 47, 145, 273, 1843.

[9] G. A. Kenngott, *Die Minerale der Schweiz nach ihren Eigenschaften und Fundorten*, Leipzig, 366, 1866.

[10] V. von Zepharovich, *Mineralogisches Lexicon für das Kaiserthum Œsterreich*, Wien, 280, 1859; 210, 1873; A. Model, *Tschermak's Mitt.*, (2), **13**. 532, 1892; E. Fugger, *Die Mineralien des Herzogthums Salzburg*, Salzburg, 16, 1878; A. Kittl, *Centr. Min.*, 143, 1914; J. Königsberger, *ib.*, 493, 1914.

[11] T. C. F. Hall, *Lead Ores*, London, 78, 1921; D. A. Wray, *Geology and Mineral Resources of the Serb-Croat-Slovene State*, London, 63, 1921.

[12] E. de Hautpick, *Min. Journ.*, **98**. 678, 1912; N. von Kokscharoff, *Materialien zur Minera-*

logie Russlands, St. Petersburg, **5**. 191, 1869 ; C. C. von Leonhard, *Handbuch einer allgemeinen topographischen Mineralogie*, Frankfurt, 396, 1843 ; L. von Mühlen, *Die Lagerstätten von Wolfram, Zinn, und Molybdän in Rüssland*, Stuttgart, 1926 ; K. Nenadkewitsch, *Trav, Musée Geol. St. Petersburg*, **1**. 81, 1907 ; M. Rusakoff, *Bull. Com. Geol. Leningrad*, **44**. 1, 1926 ; Anon., *Mining Journ.*, **98**. 678, 1912 ; G. A. Meerson, *Zhur. Prikladnoi Khim. Moscow*, **2**. 133, 1929 ; V. S. Tropmoff, *Mineral'noe Suir'e i Tzvetnuie Met.*, **4**. 1122, 1929.

[13] J. J. Sederholm, *Eng. Min. Journ.*, **113**. 161, 1922 ; Anon., *Journ. Soc. Chem. Ind.-Chem. Ind.*, **38**. 457, R, 1919 ; N. von Kokscharoff, *Materialien zur Mineralogie Russlands*, St. Petersburg, **2**. 271, 1857 ; N. Nordenskjöld, *Beskrifning ofver de i Finland funna Mineralier*, Helsingfors, 1855 ; K. Nenadkewitsch, *Trav. Musée Geol. St. Petersburg*, **1**. 81, 1907 ; R. Brauns, *Centr. Min.*, 97, 1908.

[14] R. Beck, *The Nature of Ore Deposits*, New York, 209, 1905 ; C. Brauns, *Die nutzbaren Mineralien im deutsches Reiche*, Berlin, 565, 1906 ; K. Schlier, *Oesterr. Zeit. Berg. Hütt.*, **59**. 475, 1911 ; V. von Zepharovich, *Mineralogisches Lexicon für das Kaiserthum Oesterreich*, Wien, 280, 1859 ; 211, 1873 ; K. Schlier, *Oesterr. Zeit. Berg. Hütt.*, **59**. 475, 1911 ; F. Sandberger, *Neues Jahrb. Min.*, 836, 1867 ; 167, 1877 ; A. Knop, *ib.*, 43, 1858 ; C. C. von Leonhard, *Handbuch einer allgemeinen topographischen Mineralogie*, Frankfurt, 393, 1843 ; O. Luedecke, *Die Minerale des Harzes*, Berlin, 103, 1896 ; H. Traube, *Die Minerale des Schlesiens*, Breslau, 145, 1888 ; G. Woitschach, *Das Granitgebirge von Königshain*, Breslau, 43, 1881 ; W. von Gümbel, *Geognostische Beschreibung des Bayern*, Gotha, **2**. 306, 1868 ; **3**. 300, 1879 ; A. Krause, *Schles. Ges. vaterl. Cult.*, 52, 1847 ; A. Frenzel, *Mineralogisches Lexicon für das Königreich Sachsen*, Leipzig, 207, 1874 ; G. A. Kenngott, *Uebersicht der Resultate mineralogischer Forschungen*, Leipzig, 170, 1857 ; W. Harres, *Zeit. Kryst.*, **11**. 112, 1886 ; *Notizbl. Ver. Erdkunde Darmstadt*, 2, 1881 ; 3, 1882.

[15] F. J. Stephens, *Trans. Inst. Min. Met.*, **27**. 198, 1918 ; S. H. Ball, *Eng. Min. Journ.*, **104**. 333, 1917 ; C. C. von Leonhard, *Handbuch einer allgemeinen topographischen Mineralogie*, Frankfurt, 396, 1843 ; M. Sorg, *Zeit. prakt. Geol.*, **27**. 35, 1919.

[16] W. C. Brögger, *Zeit. Kryst.*, **16**. 5, 1890 ; H. H. Claudet, *Bull. Canadian Min. Inst.*, **51**. 609, 1916 ; T. Scheerer, *Neues Jahrb. Min.*, 643, 1843 ; 233, 1846 ; M. Hörnes, *ib.*, 785, 1846 ; S. Blekum, *Tids. Kemi Bergvaesen*, **3**. 102, 1923 ; A. Hasselborn, *Montan Ztg.*, **16**. 234, 1909 ; B. Dammer and O. Tietze, *Die nutzbaren Mineralien*, Stuttgart, **1**. 113, 1913 ; E. O. Falkenberg, *Eng. Min. Journ.*, **111**. 1021, 1921 ; V. M. Goldschmidt, *Die Kontaktmetamorphose im Kristiangebiet*, Kristiania, 1911 ; E. R. Woakes, *Trans. Inst. Min. Met.*, **27**. 184, 1918 ; C. C. von Leonhard, *Handbuch einiger allgemeinen topographischen Mineralogie*, Frankfurt, 395, 1843.

[17] A. E. Fersman, *Ore Messenger*, **1**. 78, 1916.

[18] A. K. Coomaraswamy, *Rep. Min. Surrey Ceylon*, 4, 1905 ; Anon., *Bull. Imp. Inst.*, **6**. 181, 1908.

[19] J. C. Brown and A. M. Heron, *Rec. Geol. Sur. India*, **50**. ii, 101, 1919 ; J. M. Campbell, *Min. Mag.*, **20**. 85, 1919.

[20] D. N. Wadia, *Geology of India*, London, 1919 ; J. C. Brown, *Bull. Indian Indus. Labour*, 19, 1921 ; G. H. Tipper, *Rec. Geol. Sur. India*, **52**. 305, 1921.

[21] W. R. Jones, *Trans. Inst. Min. Met.*, **29**. 320, 1920 ; T. Pakliang, *Recherches sur quelques minerais chinois de tungstene et de molybdène*, Paris, 1928.

[22] K. Jimbo, *Journ. Coll. Science Tokyo*, **11**. 213, 1899 ; S. Kozu and W. Watanabe, *Proc. Pan-Pacific Science Congr.*, **3**. i, 839, 1926.

[23] E. du Hautpick, *Min. Journ.*, **98**. 678, 1912.

[24] J. Barthoux, *Bull. Soc. Min.*, **47**. 36, 1924 ; G. Castelli, *Rassegna Mineraria*, **62**. 101, 125, 1925 ; R. A. Farquherson, *First Report on the Geology and Mineral Resources of British Somaliland*, London, 1924.

[25] J. D. Falconer, *Bull. Geol. Sur. Nigeria*, **1**. 23, 34, 1921.

[26] H. B. Maufe, *South Rhodesia Geol. Sur.*, 12, 1921.

[27] P. A. Wagner, *Mem. Geol. Sur. Union S. Africa*, **7**. 111, 1916 ; W. Versfeld, *Mem. Geol. Sur. Union S. Africa—Dept. Mines*, **1**. 62, 1919 ; Anon., *Iron Coal Trades Rev.*, **93**. 42, 1916.

[28] A. W. Rogers and A. L. du Toit, *Geology of Cape Colony*, London, 477, 1909 ; A. L. du Toit, *S. African Journ. Science*, 153, 1916 ; Anon., *Bull. Imp. Inst.*, **13**. 501, 1915 ; J. P. Johnson, *The Mineral Industry of Rhodesia*, London, 39, 1911 ; *Trans. Geol. Soc. S. Africa*, **10**. 115, 1911 ; H. Merensky, *ib.*, **11**. 31, 1908 ; F. H. Hatch, *Report on the Mines and Mineral Resources of Natal*, London, 87, 1910.

[29] A. L. Parsons, *Ontario Bur. Mines*, **26**. 275, 1917 ; *Canada Min. Journ.*, **38**. 231, 1917 ; E. Poitevin and R. P. D. Graham, *Bull. Museum Canada Geol. Sur.*, 27, 1918 ; T. L. Walker, *Canada Dept. Mines*, 93, 1911 ; J. C. Guillim, *Rept. Canada Munition Conm.*, 108, 1920 ; W. E. Hidden, *Amer. Journ. Science*, (3), **32**. 204, 1886 ; G. C. Hoffmann, *Ann. Rep. Geol. Sur. Canada*, **9**. 16, 1898 ; *Annotated list of Minerals occurring in Canada*, Ottawa, 92, 1890 ; *Trans. Roy. Soc. Canada*, **7**. 65, 1890 ; C. W. Drysdale, *Rept. Canada Geol. Sur.*, 54, 1916 ; *Bull. Canadian Min. Inst.*, **43**. 872, 1915 ; J. J. O'Neill, *Mem. Canada Geol. Sur.*, **110**. 12, 1919 ; F. D. Adams and A. E. Barlow, *ib.*, **6**. 87, 1910 ; E. L. Bruce, *Rept. Canada Geol. Sur.*, 22, 1917 ; C. Camsell, *ib.*, 207, 1916 ; B. C. Lamble, *Trans. Canadian Min. Inst.*, **22**. 61, 1919 ; J. S. de Lury, *Canadian Min. Journ.*, **38**. 460, 1917 ; R. O. Sweezey, *ib.*, **34**. 190, 1913 ; A. Mailhiot, *ib.*, **41**. 135, 1920 ; *Rept. Quebec Min. Operations*, 40, 1919 ; M. E. Wilson, *Canadian Min. Journ.*, **39**. 78, 84, 1918 ; *Eng. Min. Journ.*, **109**. 655, 1920 ; W. H. Smith, *ib.*, **99**. 271, 1915 ; J. A. Dresser, *ib.*, **103**. 494, 1917 ; E. Thomson, *Econ. Geol.*, **13**. 302, 1918 ; C. W. Cook, *ib.*, **20**. 185, 1925 ; V. L. Eardley-

Wilmot, *Molybdenum*, Ottawa, 1925; *Chem. Trade Journ.*, **78**. 91, 1926; Anon., *Chem. Met. Engg.*, **19**. 654, 1918; J. A. Dresser, *Bull. Canadian Min. Inst.*, **59**. 206, 1917; *Min. Journ.*, **116**. 161, 1917; W. H. Smith, *Eng. Min. Journ.*, **99**. 271, 1915; H. E. Wood, *Trans. Canadian Min. Inst.*, **19**. 106, 1916; H. H. Claudet, *ib.*, **19**. 124, 1916; F. J. Stephens, *Trans. Inst. Min. Met.*, **27**. 198, 1918; E. S. Larsen and C. S. Ross, *Econ. Geol.*, **15**. 567, 1920; W. Gerrie, *Geol. Stud. Univ. Toronto*, 24, 1927; H. F. Evans, *Mining World*, **23**. 443, 1916.

[30] F. W. Horton, *Bull. U.S. Bur. Mines*, 111, 1916; T. Chapin, *Bull. U.S. Geol. Sur.*, 692, 1919; G. L. Harrington, *ib.*, 683, 1918; F. C. Calkins, *ib.*, 640, D, 1916; F. L. Hess, *ib.*, 340, 1908; 750, 761, 1924; G. O. Smith, *ib.*, 260, 1904; W. H. Emmons, *ib.*, 432, 1910; G. A. Smith, *ib.*, 260, 1905; F. C. Schrader and J. M. Hill, *ib.*, 430, 1910; F. C. Schrader, *ib.*, 750, 1924; *Econ. Geol.*, **12**. 237, 1917; E. S. Larson and C. S. Ross, *ib.*, **5**. 567, 1920; J. F. Kemp and P. Billingsley, *ib.*, **13**. 257, 1918; B. W. Hitts, *Min. World*, 323, 1909; A. R. Crook, *Bull. Amer. Geol. Soc.*, **15**. 283, 1904; L. W. Wickers, *Min. Scien. Press*, **114**. 699, 1917; C. C. von Leonhard, *Handbuch einer allgemeinen topographischen Mineralogie*, Frankfort, 396, 1843; F. A. Genth, *The Minerals of North Carolina*, Washington, 23, 1891; G. A. Koenig, *Proc. Acad. Philadelphia*, 38, 1887; H. W. Turner, *Amer. Journ. Science*, (4), **5**. 427, 1898; W. E. Hidden and J. B. Mackintosh, *ib.*, (3), **38**. 485, 1889; W. P. Blake, *Annotated Catalogue of the Principal Minerals in California*, Sacramento, 1866; H. Fleck, *Proc. Colorado Scient. Soc.*, **11**. 103, 1916; D. F. Haley, *Trans. Amer. Inst. Min. Eng.*, **61**. 71, 1920; H. L. Brown and M. W. Haywood, *Eng. Min. Journ.*, **105**. 905, 1918; H. F. Yancey, *Chem. Met. Engg.*, **19**. 186, 1918; E. S. Larson and C. S. Russ, *Econ. Geol.*, **15**. 567, 1920; L. W. Staples and C. W. Cook, *Amer. Min.*, **16**. 1, 1931; L. F. S. Holland, *Min. Scient. Press*, **117**. 529, 1918; P. G. Worcester, *Bull. Colorado Geol. Sur.*, **14**. 87, 1919.

[31] A. F. Buddington, *Econ. Geol.*, **25**. 197, 1930; T. Chapin, *Bull. U.S. Geol. Sur.*, 692, 1919; J. B. Mertie, *ib.*, 714, 1919; F. L. Hess, *ib.*, 761, 1924.

[32] Anon., *Bull. Imp. Inst.*, **6**. 181, 1908.

[33] J. B. Ferguson, *Amer. Journ. Science*, (4), **37**. 399, 1914; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, 167, 1900.

[34] J. F. Kemp, *Trans. Amer. Inst. Min. Eng.*, **36**. 195, 1906; F. L. Hess, *Bull. U.S. Geol. Sur.*, 652, 1917; C. F. de Landero, *Sinopsis mineralogica ó catalogo descriptivo de los minerales*, Mexico, 340, 1888.

[35] J. E. Clennell, *Amer. Journ. Science*, (4), **37**. 170, 1914.

[36] B. L. Miller and J. T. Singewald, *The Mineral Deposits of South America*, New York, 1919.

[37] Anon., *Mineral Industry*, 514, 1916.

[38] I. Domeyko, *Elementos de mineralojia*, Santiago, 87, 1879; B. L. Miller and J. T. Singewald, *The Mineral Deposits of South America*, New York, 1919.

[39] E. I. Daenas, *Bol. Cuerpo Ing. Minas Peru*, 35, 1906; E. Weckwarth, *ib.*, 63, 1908; *Mining Journ.*, **85**. 523, 1909; A. Raimondi, *Minéraux du Pérou*, Paris, 183, 1878.

[40] C. C. von Leonhard, *Handbuch einer allgemeinen topographischen Mineralogie*, Frankfurt, 396, 1843.

[41] F. Schrader and J. M. Hill, *Mining World*, **33**. 185, 1910.

[42] E. C. Andrews. *Min. Resources N.S.W. Geol. Sur.*, 11, 1906; 24, 1916; *Mining Mag.*, **14**. 291, 1916; J. E. Carne and E. C. Andrews, *Ann. Rept. N.S.W. Dept. Mines*, 176, 1915; M. Morrison, *ib.*, 109, 111, 1920; E. J. Kenny, *Bull. Dept. Mines. Geol. Sur. N.S.W.*, 5, 1924; A. Liversidge, *Proc. Roy. Soc. N.S.W.*, **29**. 316, 1895.

[43] G. J. Gray and R. J. Winters, *Bull. Northern Territory*, 15, A, 1916; T. G. Oliver, *ib.*, 8, 1916.

[44] E. C. S. Smith, *Publ. Queensland Geol. Sur.*, 243, 1914; *Queensland Govt. Min. Journ.*, **15**. 184, 1914; **18**. 345, 1917; B. Dunstan, *ib.*, **17**. 314, 1916; **21**. 462, 504, 1920; L. C. Ball, *ib.*, **14**. 4, 1913; **16**. 503, 1915; *Publ. Queensland Govt. Geol. Sur.*, 248, 1915; J. H. Reed, *ib.*, 465, 1919; *Eng. Min. Journ.*, **110**. 947, 1920.

[45] R. L. Jack, *Bull. S.A. Geol. Sur.*, **6**. 44, 1917.

[46] H. Herman, *Rec. Victoria Geol. Sur.*, **4**. ii, 169, 1920; P. T. L. Kenny, *ib.*, **4**. iii, 296, 1921; *Chem. Eng. Min. Rev.*, **13**. 448, 1920; G. H. F. Ulrich, *Contributions to the Mineralogy of Victoria*, Melbourne, 7, 1870.

[47] A. G. Maitland, *Mem. Geol. Sur. West Australia*, 1, 1919; E. S. Simpson, *Bull. W. Australia Geol. Sur.*, 59, 1914.

[48] E. C. Edwards, *Mineral Resources New South Wales*, Sydney, 11, 1906; E. C. Andrews, *Min. Mag.*, **14**. 291, 1916; *New South Wales Dept. Mines*, 24, 1916.

[49] L. Hills, *Min. Resources, Tasmania Geol. Sur.*, 1, 1916; L. L. Waterhouse, *ib.*, 1, 1916; *Bull. Tasmania Geol. Sur.*, **21**. 181, 1916; W. H. Twelvetrees, *ib.*, 9, 1911; 14, 1913; A. McIntosh Reid, *ib.*, 29, 1919; W. F. Petterd, *Catalogue of the Minerals of Tasmania*, Hobart, 1910.

[50] F. B. Allen, *New Zealand Mines Record*, **6**. 422, 1903; S. Fry, **8**. 369, 1905; E. J. H. Webb, *Bull. New Zealand Geol. Sur.*, (2), **11**. 26, 1910; Anon., *Journ. Ind., Eng. Chem.*, **8**. 850, 1916; S. Fry, *Mining World*, **23**. 363, 1905.

[51] R. H. Rastall, *Molybdenum Ores*, London, 1922; *Chem. Trade Journ.*, **87**. 5, 1923; L. Moser, *Oesterr. Chem. Ztg.*, **26**. 67, 1923; V. L. Eardley-Wilmot, *Molybdenum*, Ottawa, 1925; *Chem. Trade Journ.*, **78**. 91, 1926; A. H. Hunter, *Blast Furnace*, **9**. 356, 426, 1921; *Iron Age*, **107**. 1469, 1511, 1921; H. H. Smidt, *Tids. Kemi Bergvesen*, **8**. 66, 1928.

[52] M. Spica, *Gazz. Chim. Ital.*, **24**. i, 97, 1894.

[53] W. F. Hillebrand, *Chem. News*, **78**. 216, 1898; *Bull. U.S. Geol. Sur.*, 167, 1900; *Amer. Journ. Science*, (4), **6**. 209, 1899; J. B. Ferguson, *ib.*, (4), 37, 399, 1914; M. Spica, *Gazz. Chim. Ital.*, **24**. i, 97, 1894; C. J. Heine, *Journ. prakt. Chem.*, (1), **9**. 204, 1836; C. D. Braun, *Zeit. anal. Chem.*, **6**. 86, 1863; C. R. Fresenius and E. Hintz, *ib.*, **24**. 412, 1885; F. Wöhler, *Der Mineralanalyse in Beispielen*, Göttingen, 1861; P. Krusch, *Zeit. prakt. Geol.*, **27**. 76, 1919; H. Traube, *Neues Jahrb. Min. B.B.*, **7**. 232, 1892; F. Zambonini, *Amer. Min.*, **12**. 1, 1927; H. St. C. Deville, *Compt. Rend.*, **49**. 210, 1859; H. Ramage, *Nature*, **119**. 783, 1927; W. B. Giles, *Chem. News*, **76**. 137, 1897; T. L. Phipson, *ib.*, **65**. 217, 1892; C. de B. Evans, *Journ. Chem. Soc.*, **93**. 666, 1908; A. Scacchi, *Atti Accad. Napoli*, **18**. 296, 1879; A. Jorissen, *Bull. Soc. Chim. Belg.*, **27**. 21, 1913; W. Steinkuhler, *ib.*, **32**. 233, 1923; L. A. Palmer, *Journ. Amer. Cer. Soc.*, **12**. 37, 1929; K. Chudoba, *Centr. Min.*, 11, 1929.

[54] E. Demarçay, *Compt. Rend.*, **130**. 91, 1900; F. von Oefele, *Pharm. Centrh.*, **46**. 683, 1905.

§ 3. The Extraction of Molybdenum

The molybdenum ores are first concentrated.[1] In the case of wulfenite ores, this operation is comparatively simple because the mineral has a high sp. gr. and is easily wetted. Hence, water separation can be employed for removing the gangue. Pneumatic concentration has also been used when water is scarce. Molybdenite is not usually treated by water separation because the flaky mineral is not easily wetted, and it is liable to float. The ores are poor—over 2 per cent. of molybdenite is rare. The electrostatic process can be employed with ore rather coarsely crushed. The ore is dried and warmed. Other sulphides also collect with the molybdenite, and the flotation process is the most successful mode of concentrating the ore. Water flotation is used in some cases, but oil flotation—in different forms—is more generally employed.

The extraction of molybdates or molybdic acid.—F. Wöhler,[2] and J. J. Berzelius recommended roasting the sulphide in a current of air so as to collect the sublimate of molybdenum trioxide. C. Brunner roasted an intimate mixture of the sulphide with sand, with stirring until the mass became yellow. The molybdic acid was extracted with aq. ammonia; and the unoxidized residue was roasted again. The ammoniacal soln. was treated with a little ammonium hydrosulphide to precipitate the copper; the filtrate was evaporated to dryness; extracted with dil. ammonia; and the filtrate evaporated for the crystallization of ammonium molybdate. R. W. Stimson, C. Svensson, and L. F. Svanberg and H. Struve used modifications of the process. F. Luchs deflagrated a mixture of potassium nitrate and molybdenite, extracted the mass with water, and treated the product with nitric acid. A. Kissock roasted a mixture of the sulphide with lime.

K. Christl melted a mixture of powdered wulfenite and sodium carbonate, and poured out the molten mass so that the alkali molybdate was separated as much as possible from the lead oxide. The cold cake was extracted with hot water. The filtrate was treated with a little ammonia and ammonium carbonate to precipitate lead carbonate; and the filtrate was mixed with nitric acid and evaporated to dryness. The sodium nitrate was removed from the molybdic acid by extraction with water. C. Elbers modified the process by adding iron turnings or carbonized potassium tartrate to the original mixture. This reduces the lead to the metal, but not the molybdic acid. A. Kissock roasted the ore mixed with a calcium salt, so as to form calcium molybdate and, similarly, by roasting with ferric oxide or sulphide, ferric molybdate is formed. The product was then treated for molybdic acid. J. W. Weitzenkorn heated a mixture of molybdenite with manganese oxide in the presence of oxygen. F. D. S. Robertson roasted the sulphide ore to oxide, and then volatilized the molybdenum trioxide. B. Broch, and P. Schwarzkopf heated the ore at 1100°–1500° in dry oxygen to volatilize the trioxide; and S. Westberg and E. Edwin first reduced the ore with hydrogen before the oxygen treatment. E. K. Jenckes leached roasted molybdenite with aq. ammonia; precipitated iron, copper, and calcium from the soln.; and this, when crystallized, furnished ammonium molybdate. Guggenheim Bros. heated the ores in a gas containing sulphur—*e.g.* sulphur vapour, hydrogen or carbon sulphides—so as to form a volatile sulphide. G. D. van Arsdale and co-workers washed the roasted ore with dil. sulphuric acid, treated it with alkali-lye to form alkali molybdate, and regenerated the alkali-lye at the anode. F. L. Hahn and W. Franke heated the molybdate at 250° to 300° with carbon tetrachloride under press., and extracted the product with acid.

F. Ullik washed the wulfenite ore with dil. hydrochloride acid to remove carbonates, phosphates, oxides, etc. ; the washed product was digested with hot, conc. hydrochloric acid ; the soln. was concentrated and cooled to separate lead chloride ; and the remaining lead precipitated as lead sulphate ; or else the soln. was evaporated to dryness, and the molybdenum compound extracted with aq. ammonia as recommended by F. Wöhler. Basic lead chloride remained. Ammonium molybdate was crystallized from the soln. ; or else the soln. was evaporated with nitric acid, and the ammonium nitrate removed from the molybdic acid by washing with water. H. Debray purified the ammonium molybdate by heating to redness a mixture with an equal amount of ammonium chloride, and roasting the product. The purification of molybdenum salts is discussed in memoirs dealing with the at. wt. (*q.v.*). C. Elbers decomposed wulfenite by heating it with conc. sulphuric acid ; and after evaporation, the blue liquid was diluted with water. The filtrate from the lead sulphate was mixed with nitric acid and evaporated. Molybdic acid separated out, and this was washed with water acidulated with nitric acid. The filtrate was again diluted and treated with nitric acid to recover more molybdic acid. W. Delffs, and A. Rodland decomposed the mineral with nitric acid, but C. Elbers, and A. von Wich did not recommend the process.

L. A. Buchner and F. Mahla heated a mixture of wulfenite and carbon in a current of chlorine, and extracted the molybdenum chloride with alcohol. P. Nicolardot opened up the wulfenite by fusion with potassium hydrosulphate ; extracted the cold mass with water ; evaporated the soln. to dryness ; and heated the product with carbon and sulphur to form molybdenum disulphide. F. Wöhler heated a mixture of wulfenite, carbonized sodium tartrate, and sulphur ; dissolved the sodium sulphomolybdate in water, and on treating the soln. with sulphuric acid, molybdenum trisulphide was precipitated. This was washed, dried, and heated out of contact with air. The resulting molybdenum disulphide was roasted for molybdenum trioxide. G. E. Mauritii obtained the sulphomolybdate by boiling the mineral with potassium carbonate and sulphur ; F. Wöhler, with soda-lye and sulphur ; G. C. Wittstein, with sodium polysulphide ; and W. Wicke, with aq. ammonium sulphide.

According to J. P. Bonardi, when wulfenite is first concentrated, the concentrate contains 15 to 20 per cent. of MoO_3. The vanadinite, cerussite, anglesite, galena, pyromorphite and mimetite collect in the concentrate. The ore can then be treated with an acid or an alkaline leach, or fused with something which will reduce the lead to the metallic form and leave the molybdenum in the slag. The acid leach is the least favourable process. The sodium sulphide leach has proved most satisfactory. The molybdenum passes into soln. as sodium molybdate, the lead and precious metals collect in the residues. The sodium molybdate can then be used for the preparation of ferromolybdenum, etc. If the concentrate be fused with soda-ash, caustic soda, and coal, the lead is recovered as bullion, and the sodium molybdate can be leached from the slag. The subject was discussed by R. E. Head and V. Miller.

R. E. Pearson and co-workers [3] proposed an electrolytic process for extracting the molybdenum. The ore is ground and mixed to a paste with sulphuric acid, and the mixture is replaced on a lead plate which forms the anode of an electrolytic cell containing dil. sulphuric acid. On passing a current through the cell the basic impurities, *e.g.* iron, manganese, calcium or sodium oxide, in the material on the anode pass into soln., leaving a residue of tungsten or molybdenum oxides. Alternatively the anode may consist of nickel or a nickel alloy, and the electrolyte of caustic soda, whereby soluble sodium tungstate or molybdate is formed and the foreign metals are left as anode slime.

In working up molybdenum residues which collect in the determination of phosphates in the analysis of manures, steel, etc., the molybdic acid has to be separated from phosphates. J. A. Prescott[4] evaporated the soln. to dryness; dissolved the residue in aq. ammonia; and treated the soln. with magnesia mixture to precipitate the phosphoric acid. The soln. was then evaporated to allow the ammonium molybdate to crystallize, and the mother-liquors worked up with a subsequent collection of molybdenum residues. Processes were also described by C. R. Fresenius, F. Muck, O. Maschke, H. Uelsmann, E. Reichardt, A. Gawalowsky, A. Bornträger, W. D. Brown, R. Friedrich, H. Kinder, P. Rudnik and R. D. Cooke, C. G. Armstrong, H. Rubricius, E. Stamm, etc. V. Lenher and M. P. Schultz diluted the waste molybdate liquor, or treated it with alkali so that the amount of free nitric acid is reduced to 0·1–0·4 per cent. Hydrogen sulphide is then passed into the soln., preferably warm, and the precipitated molybdenum sulphide is washed and dried, after which it may be converted into the trioxide by roasting. Again, ammonium phosphomolybdate is dissolved in sufficient aq. sodium hydroxide to make a soln. just alkaline to phenolphthalein; the liquid, after filtration if necessary, is treated with hydrogen sulphide, and the molybdenum sulphide precipitated by acidifying with dil. hydrochloric acid.

The preparation of the element.—J. J. Berzelius,[5] F. Wöhler, C. F. Rammelsberg, C. W. Blake, J. H. Müller, P. Sabatier and J. B. Senderens, L. F. Svanberg and H. Strüve, and H. N. Warren, obtained the metal by heating molybdenum trioxide to a high temp. in a current of *hydrogen.* Since this oxide is volatile at a high temp. as pointed out by H. Debray, and A. Rogers and F. H. Mitchell, it is better to work at a lower temp. at first so as to make the less volatile lower oxides, and reduce these at the higher temp. M. Guichard said that the reduction to the brown dioxide begins at 300°, and the dioxide begins to reduce at about 500°, and is fairly rapid at 600°. The sole product of the reduction is molybdenum—the incompletely reduced portion is a mixture of molybdenum and its dioxide. Finely-divided molybdenum is not appreciably oxidized by steam at temp. below 700°. Consequently, the steam produced by the action of hydrogen on the oxides of molybdenum at 600–700° has no tendency to reverse the action, and may be considered as an inert gas; above 700°, however, it is a reagent and the inverse change becomes possible. When molybdenum and its dioxide are heated at these temp. in a mixture of hydrogen and steam, both reactions, oxidation and reduction, occur simultaneously, and the state of equilibrium finally attained: $MoO_2+2H_2 \rightleftharpoons Mo+2H_2O$ depends on the partial press. of the constituents of the gaseous mixture. The metal or its dioxide is not affected at 800° by a current of the gaseous mixture containing its constituents in approximately molecular proportion; when the proportion of steam is larger than this, the metal is almost wholly oxidized to dioxide, whilst excess of hydrogen brings about a complete reduction of the oxide. L. Meyer and H. Haas, and L. P. Liechti and B. Kempe found that it is difficult to remove all the oxygen from the reduced metal by hydrogen and they said that the last traces of oxygen can be removed by dry hydrogen chloride at 200°, but A. Vandenberghe, and M. Guichard showed that molybdenum dioxide does not volatilize when heated in hydrogen chloride. There is a difficulty in obtaining a suitable vessel for the reduction, to avoid contaminating the molybdenum, since, as was shown by O. von der Pfordten, and by A. Vandenberghe, that metal reacts at a high temp. with platinum, and porcelain. A. Vandenberghe found that an old porcelain vessel gave the best results since it acquired a protective film of metal from previous reductions. E. W. Engle preferred the hydrogen reduction process when the metal of a high degree of purity is required. The reduction of molybdenum trioxide commences at about 300°. J. H. Müller used a quartz vessel. H. N. Warren used a tube of compressed lime as container. Some impurities can be removed by washing the molybdenum powder with hydrofluoric acid, hydrochloric acid, and water. F. Wöhler and L. von Uslar reduced molybdenum chloride at a red-heat by means of hydrogen. O. von der Pfordten reduced molybdenum sulphide or molybdenite in the same way—but A. Vandenberghe added that the method is useful only when small quantities have to be reduced. A. E. van Arkel obtained molybdenum by heating a filament of the metal in an atmosphere of an easily dissociated volatile compound.

Most of the molybdenum compounds are reduced by *carbon* at a high temp., and although there is a tendency to form a carbide, a metal of a high degree of purity can be so obtained. Thus, P. J. Hjelm, C. F. Bucholz, and J. J. Berzelius reduced molybdenum trioxide, or acid potassium molybdates by heating a white-hot admixture with carbon in a carbon crucible ; and H. Debray added that the product contains 4 to 5 per cent. of carbon which makes the metal more fusible than if it were pure. E. D. Clarke obtained molybdenum by reducing it in the oxyhydrogen blowpipe flame. A. Sternberg and A. Deutsch reduced alkaline earth molybdates by heating them with carbon at 1000° to 1400° ; carbon monoxide is evolved, and the alkaline earth oxide can be removed from the product by hydrochloric acid. According to A. Vandenberghe, with calcium molybdate, the product contained 3 per cent. of carbon. If alkali molybdates are used, the alkali metal is also formed. H. Moissan prepared molybdenum as follows : Molybdenum dioxide, prepared by strongly heating ammonium molybdate, is mixed with one-tenth of its wt. of sugar carbon, and heated for about six min. in a carbon crucible in an arc produced by a current of 800 ampères and 60 volts. With the proportions given, the molybdenum oxide is in excess, and if the action of the arc is stopped before the outer portions of the mixture in contact with the crucible have had time to fuse, molybdenum is obtained quite free from carbon, and containing only from 0·1 to 0·2 per cent. of slag as an impurity. If, however, the action of the arc is prolonged until the whole mixture fuses, the crucible is attacked, and, on cooling, a hard, brittle ingot of carboniferous molybdenum is obtained. A. Vandenberghe found 0·28 per cent. of carbon in the molybdenum obtained under the former conditions. The Ampère Gesellschaft obtained molybdenum by melting a mixture of calcium molybdate, molybdenite, and carbon. M. Guichard reduced molybdenite by H. Moissan's process ; and C. Lehmer, by electrolytically heating a mixture of molybdenite with carbon and calcium oxide : $MoS_2+2CaO+2C=Mo+2CaS+2CO$. O. W. Brown reduced molybdenite by carbon and calcium oxide in an electrically heated furnace : $MoS_2+2C+2CaO=Mo+2CaS+2CO$. J. N. Pring and W. Fielding reduced molybdenum tetra- and penta-chlorides by carbon at a temp. below 1300° ; above that temp., carbide was formed. J. E. Loughlin obtained a small yield of molybdenum by heating for 12 hrs. at a white-heat a mixture of molybdenum trioxide with $1\frac{1}{2}$ times its wt. of *potassium cyanide* in a luted porcelain crucible contained in a larger crucible with the intermediate space packed with animal charcoal.

W. Muthmann and co-workers obtained the metal by melting in an electric furnace at a high temp. a mixture of molybdenite, calcium oxide, in the molar proportions 3 : 4 along with calcium fluoride as a flux. A. B. du Jassonneix reduced molybdenum oxide with *boron* in a magnesia crucible in an electric furnace ; and B. Neumann heated electrically a bath of alumina and lime to which was added molybdenum trioxide and *silicon*. The product contained about 2 per cent. of silicon and a little carbon. L. Kahlenberg and W. J. Trautmann studied the reduction of the trioxide and of molybdates by silicon. A. Burger, H. Kuzel and E. Wedekind, and E. Wedekind and O. Jochem found that molybdenum trioxide in an iron boat in vacuo is reduced by the vapour of *calcium*—the product obtained by the reduction of the oxide with calcium, contained 2 to 3 per cent. of calcium ; with *zinc* as reducing agent, a little iron is usually present. E. Wedekind and O. Jochem found that the metal is produced in a powdered form. W. Prandtl and B. Bleyer used a mixture of calcium and aluminium ; and O. P. Watts and J. M. Breckenridge, an alloy of calcium, magnesium, and aluminium. A. Stavenhagen and co-workers, H. J. Braun, J. J. Boericke, H. Biltz and R. Gärtner, and H. Lohmann found that the *aluminium* thermite process can be used for the reduction of molybdenum oxide. The most common method for preparing molybdenum commercially is to reduce molybdenum concentrate or molybdenite with finely-divided aluminium. The metal may contain 1 to 2 per cent. of iron, and a small proportion of silicon. A. Rosenheim and H. J. Braun obtained a good yield of metal, free from air-bubbles, by moderating the reaction by the addition of a flux of 50 parts of calcium fluoride for every 100 parts of molybdenum trioxide and 38 parts of aluminium, and allowing the metal to agglomerate by keeping the mass in a liquid condition for some time after the reaction. W. Lederer said that owing to the reactivity of the molybdenum, the heating of the metal should not be prolonged more than is necessary. L. Weiss and O. Aichel used *Mischmetal* as the reducing agent in place of aluminium. The metal of a high degree of purity was prepared by C. Müller and W. Schubardt, by heating the carbonyl.

In 1803, J. G. Gahn noticed the separation of molybdenum in the electrolysis of a soln. of ammonium molybdate—*vide infra*, molybdenum trioxide; and in 1815, J. G. Children obtained some molybdenum by the electro-reduction of molybdenum trioxide; M. Junot, by the electrolysis of a soln. of molybdenum trioxide in molten potassium cyanide; the Wolfram Lampen A. G., by the electrolysis of soln. of say molybdenum hexachloride in an organic solvent like acetone using a platinum or nickel cathode; and L. Ott, by the electrolysis of molten molybdates mixed with molybdenum trioxide. H. Mennicke discussed the commercial preparation of the metal. E. W. von Siemens and J. G. Halske deposited molybdenum from a bath of fused salt as in the case of tungsten (*q.v.*). A. Chilesotti did not succeed in depositing molybdenum from a soln. of the trioxide in hydrochloric or sulphuric acid. L. Andrieux obtained the metal by the electrolysis of a soln. of the trioxide in a bath of borate and fluoride. J. L. Merrill and A. S. Russell found that mercury is the most suitable cathode for the deposition of molybdenum, and the best current densities are 0·6 to 1·0 amp. per sq. cm., and the best acidities, 1·2 to $1{\cdot}4N\text{-}H_2SO_4$; the time required for the deposition of a gram of molybdenum from a soln. of sodium molybdate is then about 50 min., and the time is not shortened by the use of a rotating cathode. J. Férée, A. S. Russell and S. W. Rowell, and R. E. Myers also used a mercury cathode. R. E. Pearson and E. N. Craig reduced molybdenum oxide or hydrated oxide by making it into a paste with sulphuric acid, and introducing the mixture into a porous pot surrounding a cathode consisting of a bundle of nickel-chromium alloy rods. The anode of the cell consists of a lead plate embedded in a mass of scrap molybdenum (or other easily oxidizable material) contained in a porous pot. On passing a direct current through the cell and agitating the paste surrounding the cathode, the oxide contained therein is reduced to a lower oxide from which, by suitable washing, impurities such as iron, calcium, and sodium salts may be more readily removed than from the original trioxide. At the same time, the waste metal surrounding the anode is oxidized to trioxide, which is used to make further quantities of the reduced oxide. The latter, after washing and drying, is reduced to a metallic powder by heating in a current of hydrogen in known manner. L. St. C. Broughall electrolyzed a soln. of a molybdenum salt in liquid ammonia at a low temp. or under press. C. Lehmer obtained ferromolybdenum, chromomolybdenum, nickelmolybdenum, manganomolybdenum, and cupromolybdenum by electrolytically heating a mixture of the respective metal oxide with molybdenum sulphide, calcium oxide, and carbon. L. Andrieux obtained molybdenum by the electrolysis of fused borates. Electrolytic processes for the preparation of molybdenum were described by R. E. Pearson and E. N. Craig. The preparation of ferro-molybdenum at the works of the Molybdenite Co. at Orillia, Ontario, Canada, was described by B. C. Lamble:

A wrought-iron jacket, fitted to a cast-iron base, is connected with one terminal of the electric supply. Inside the iron jacket a cubical crucible, with a tap-hole in the bottom, is built up with carbon blocks, the space between the crucible and the jacket being filled with magnesia bricks. The second electrode consists of a 10-inch graphite rod, held by a water-cooled head over the centre of the furnace. The power used is 4000 amperes at 50 volts. The smelting mixture consists of 70 per cent. molybdenite concentrate and 30 per cent. pyrite, while coke is the reducing agent and lime and silica are used as fluxes. The ferro-molybdenum produced has approximately the following composition: Molybdenum, 71·0; carbon, 3·66; sulphur, 0·08; phosphorus, 0·03; silica, 1·35; iron, 23·8 per cent. About 80 per cent. of the molybdenum in the charge is recovered in the alloy with a power consumption of 6 to 7 kilowatt-hours per lb. of alloy. The remainder of the molybdenum is recovered as dust or by wet dressing of the slag. Some analyses were also reported by A. W. Judge.

E. K. Jenckes discussed the preparation of oxides and salts of a high degree of purity for the purpose of preparing the metal for electric lamps. J. Férée obtained molybdenum by distilling in vacuo mercury from the amalgam obtained by the electrolysis of a hydrochloric acid soln. of molybdic acid using a mercury cathode. The Badische Anilin- und Sodafabrik obtained the metal by heating the nitride in vacuo. The nitride was obtained by heating molybdenum oxide, or a mixture of the oxide and the metal at 500° to 600°, in an atm. of a mixture of equal parts of hydrogen and nitrogen at 60 atm. press.

The heated metal is very reactive and is very susceptible to contamination from the containing vessel, the reducing agent, the furnace gases, and, in the electrolytic process, from the material of the electrodes. W. Lederer, and K. Wolf discussed the purification of small quantities of the metal containing, say, 3 per cent. of iron, aluminium, silicon, carbon, and oxygen. The metal is pressed into a pencil which is then heated electrically in hydrogen. The pencil is then used as an electrode in a vacuum furnace—cf. **8**. 31, 4, Fig. 1.

According to C. G. Fink,[6] **ductile molybdenum** can be prepared by methods analogous to those used for ductile tungsten, and discussed by O. Ruff, N. L. Müller, and W. D. Coolidge. P. Schwarzkopf and S. Burgstaller pressed rods from the powdered oxide, and heated them to 1100°–1150° in a current of hydrogen, and then heated them electrically to 2600°–2700° in a current of hydrogen. The resulting rods of molybdenum are ductile and can be bent into rings at a red-heat. According to O. Ruff, the ductile metal is prepared as follows:

> Molybdenum trioxide is purified by reduction at 1000° in a current of hydrogen and steam to the dioxide, which is then heated in chlorine, the oxychloride being sublimed and transferred to hydrochloric acid, when pure molybdenum trioxide is precipitated. The precipitate is washed, dried, and ignited at 1200°, when considerable shrinkage takes place. The finely-powdered product is then reduced in hydrogen at 1250°, nickel boats being used in a porcelain tube. The crystalline metal is compressed into the form of rods under about 5000 atm. press., and the brittle rods are rendered stronger by heating in hydrogen at 1300°. The presence of 0·05 per cent. of carbon is favourable. The final sintering takes place by electrical heating at a temp. of 2620°–2650°. The molybdenum contracts by about 14 per cent. The sintered rods are still quite brittle, and have to be rendered malleable and ductile by hammering at 1250° in an atm. of hydrogen. A special apparatus for the hammering is described. The hammered rods are then drawn at 400°–600° to the required size through diamond dies. The thin wires finally obtained are perfectly flexible, and may be drawn cold. The worked metal is silver-white, and does not oxidize appreciably below a red-heat.

J. Férée [7] found that the metal prepared by distilling the amalgam in vacuo is pyrophoric. A suitable reducing agent for the preparation of **colloidal molybdenum** from its salts has not been obtained. T. Svedberg obtained it by the electrical dispersion process—*vide* gold—as an *isobutylalcosol* which is brownish-black by transmitted light, and black by reflected light. H. Küzel obtained the colloidal metal by grinding or by cathodic disintegration—*vide* chromium. E. Wedekind and co-workers found that if powdered molybdenum, obtained by reducing the di- or tri-oxide by heating it with zinc, be washed in the absence of air successively with warm alcohol and warm water, then treated with dil. hydrochloric acid, and successive quantities of water added to it on a filter, an acid soln. first passes through, but later, a neutral colloidal soln. of the metal is obtained. When the precipitated metal no longer yields a colloid on washing, this property can be re-imparted to it by renewed treatment with acid. The particles of the resulting hydrosol, which keeps well if air is excluded, are negatively charged. They are immediately coagulated by alkaline electrolytes and more slowly by neutral electrolytes, but are comparatively resistant to hydrogen ions. L. Hamburger studied the properties of thin films.

REFERENCES.

[1] H. W. Bowater, *Min. Scient. Press*, **123**. 821, 1921; R. H. Rastall, *Molybdenum Ores*, London, 4, 1922; D. F. Haley, *Trans. Amer. Inst. Min. Eng.*, **60**. 14, 1918; J. W. Wells, *Min. Ind.*, 478, 1903; F. L. Hess, *Bull. U.S. Geol. Sur.*, 340, 1908; T. L. Walker, *The Molybdenum Ores of Canada*, Ottawa, 9, 1911; Metallwerk Plansee Gesellschaft, *Brit. Pat. No.* 269947, 1926; H. Alterthum, *Zeit. angew. Chem.*, **42**. 2, 1928; G. Yamada, *Month. Journ. Mining Met.*, **6**. 205, 1928; W. Hertel, *Metall Erz.*, **26**. 115, 1929; A. S. Elmore, *Eng. Min. Journ.*, **83**. 1908; 1907; H. A. Doerner, *Bull. U.S. Bur. Mines*, 399, 1926; *Eng. Min. Journ.*, **119**. 925, 1925; H. E. Wood, *ib.*, **93**. 227, 1912; W. B. Timm and C. S. Parsons, *Canada Dept. Mines*, 96, 1925; C. S. Parsons, *ib.*, 643, 1924; V. L. Eardley-Wilmot, *Molybdenum*, Ottawa, 1925; *Chem. Trade Journ.*, **78**. 91, 1926; A. H. Hunter, *Blast Furnace*, **9**. 356, 426, 1921; *Iron Age*, **107**. 1469, 1511, 1921; J. P. Bonardi, *Journ. Franklin Inst.*, **189**. 109, 123, 1920; J. B. Porter, *Rep. Geol. Sur. Canada*, **13**. 10, 1900; E. C. Andrews, *The Molybdenum Industry in New South Wales*, Sydney, 9, 1916; P. Nicolardot, *Industrie des métaux secondaires et des terres rares*, Paris, 98, 1908; H. Fleck, *Proc. Colorado Scient. Soc.*, **11**. 103, 1916; C. S. Parsons, *Canadian Dept. Mines*, 670, 1926; W. H. Rideont, *U.S. Pat. No.* 1562125, 1925; E. Pokorny, *German Pat., D.R.P.* 425364, 426431, 1923; Anon., *Metal Ind.*, **19**. 47, 1921.

[2] F. Wöhler, *Der Mineralanalyse in Beispielen*, Göttingen, 149, 1861; *Liebig's Ann.*, **45**. 374, 1843; **95**. 374, 1855; **100**. 376, 1856; C. Elbers, *ib.*, **83**. 215, 1852; F. Ullik, *ib.*, **144**. 205, 1867; L. A. Buchner and F. Mahla, *ib.*, **83**. 320, 1852; W. Wicke, *ib.*, **45**. 373, 1843; A. von Wich, *ib.*, **118**. 43, 1861; *Journ. prakt. Chem.*, (1), **84**. 73, 1861; G. E. Mauritii, *Jahrb. prakt. Pharm.*, **23**. 138, 1851; J. P. Bonardi, *Journ. Franklin Inst.*, **188**. 411, 1919; G. C. Wittstein, *Repert. Pharm.*, (2), **73**. 155, 1852; P. Nicolardot, *Industrie des métaux secondaires et des terres rares*, Paris, 106, 1908; H. A. Doerrner, *Tech. Paper U.S. Bur. Mines*, 399, 1926; A. Kissock, *U.S. Pat. No.* 1501414, 1514972, 1924; J. W. Weitzenkorn, *ib.*, 1401932, 1921; G. D. van Arsdale, R. T. and H. A. Sill, *ib.*, 1508629, 1923; P. Schwarzkopf, *ib.*, 1629004, 1927; F. D. S. Robertson, *Brit. Pat. No.*, 147470, 1920; Guggenheim Bros., 235157, 1924; A. Kissock, *ib.*, 280240, 1926; H. Debray, *Compt. Rend.*, **46**. 1095, 1858; B. Broch, *Norwegian Pat. No.* 35804, 1922; S. Westberg and E. Edwin, *ib.*, 34454, 1922; A. Rodland, *ib.*, 33720, 1922; F. L. Hahn and W. Franke, *German Pat., D.R.P.* 437561, 1925; L. F. Svanberg and H. Struve, *Svenska Akad. Handl.*, **1**. 9, 1848; *Journ. prakt. Chem.*, (1), **44**. 257, 1848; *Phil. Mag.*, (3), **33**. 409, 524, 1848; C. Brunner, *Dingler's Journ.*, **150**. 372, 1858; K. Christl, *ib.*, **124**. 398, 1852; F. Luchs, *Arch. Pharm.*, (2), **93**. 293, 1858; J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817; *Ann. Chim. Phys.*, (2), **17**. 5, 1921; *Pogg. Ann.*, **4**. 153, 1825; **6**. 331, 369, 1826; **7**. 261, 1826; W. Delffs, *ib.*, **85**. 450, 1852; C. Svensson, *Trans. Amer. Electrochem. Soc.*, **51**. 51, 1927; E. K. Jenckes, *ib.*, **51**. 387, 1927; R. E. Head and V. Miller, *Rept. Investigations Bur. Mines*, 2888, 1928; R. W. Stimson, *Brit. Pat. No.* 320845, 1928.

[3] R. E. Pearson, E. N. Craig and Durelco Ltd., *Brit. Pat. No.* 185842, 1921.

[4] J. A. Prescott, *Analyst*, **40**. 390, 1915; C. G. Armstrong, *Journ. Ind. Eng. Chem.*, **6**. 764, 1915; P. Rudnik and R. D. Cooke, *ib.*, **9**. 109, 1917; V. Lenher and M. P. Schultz, *ib.*, **9**. 684, 1917; W. D. Brown, *ib.*, **7**. 213, 1915; R. Friedrich, *Chem. Ztg.*, **40**. 560, 718, 1916; **41**. 674, 1917; H. Rubricius, *ib.*, **40**. 717, 1916; E. Stamm, *ib.*, **40**. 717, 1916; S. L. Malowan, *ib.*, **42**. 420, 1918; H. Kinder, *Stahl Eisen*, **36**. 1094, 1916; H. Debray, *Compt. Rend.*, **46**. 1095, 1858; O. Maschke, *Zeit. anal. Chem.*, **12**. 380, 1873; C. R. Fresenius, *ib.*, **10**. 204, 1871; F. Muck, *ib.*, **10**. 307, 1871; **18**. 377, 1879; H. Uelsmann, *ib.*, **16**. 52, 1877; A. Gawalowsky, *Oesterr. Chem. Ztg.*, **1**. 385, 1898; *Chem. News*, **75**. 98, 1897; A. Bornträger, *ib.*, **70**. 224, 1894; *Chem. Ztg.*, **9**. 10, 1894; E. Reichardt, *Arch. Pharm.*, (3), **2**. 232, 1873; E. Piantamida, *Giorn. Farm. Chim.*, **71**. 113, 1922; S. Holynsky, *Mem. Inst. Nat. Polonais Econ.*, **6**. A, 213, 1925.

[5] J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817; *Ann. Chim. Phys.*, (2), **17**. 5, 1921; *Pogg. Ann.*, **4**. 153, 1825; **6**. 331, 369, 1826; **7**. 261, 1826; C. F. Rammelsberg, *ib.*, **127**. 284, 1866; F. Wöhler, *Liebig's Ann.*, **94**. 372, 1855; F. Wöhler and L. Von Uslar, *ib.*, **94**. 256, 1855; W. Muthmann, L. Weiss and A. Mai, *ib.*, **355**. 100, 1907; L. Weiss and O. Aichell, *ib.*, **337**. 370, 1904; L. P. Liechti and B. Kempe, *ib.*, **169**. 344, 1873; A. Chilesotti, *Zeit. Elektrochem.*, **12**. 146, 173, 197, 1906; J. Férée, *Compt. Rend.*, **122**. 733, 1896; R. E. Myers, *Journ. Amer. Chem. Soc.*, **26**. 1129, 1904; J. L. Merrill and A. S. Russell, *Journ. Chem. Soc.*, 2389, 1929; A. S. Russell and S. W. Rowell, *ib.*, 1884, 1926; H. J. Braun, *Metallbörse*, **19**. 2190, 1929; H. Debray, *Compt. Rend.*, **46**. 1095, 1858; **56**. 732, 1863; **66**. 732, 1868; M. Guichard, *ib.*, **122**. 1270, 1896; **125**. 26, 105, 1897; **131**. 998, 1900; *Ann. Chim. Phys.*, (7), **23**. 498, 1901; *Bull. Chim. Soc.*, (3), **17**. 902, 1897; P. Sabatier and J. B. Senderens, *ib.*, (3), **7**. 503, 1892; H. Moissan, *ib.*, (3), **11**. 857, 1894; (3), **13**. 966, 1895; *Compt. Rend.*, **116**. 1225, 1893; **120**. 320, 1895; **131**. 998, 1900; **142**. 425, 1906; A. B. du Jassonneix, *ib.*, **143**. 169, 1906; H. Lohmann, *Elektrochem. Zeit.*, **25**. 141, 1918; **26**. 29, 1919; L. F. Svanberg and H. Strüve, *Svenska Akad. Handl.*, **1**. 9, 1848; *Journ. prakt. Chem.*, (1), **44**. 257, 1848; *Phil. Mag.*, (3), **33**. 409, 524, 1848; L. Meyer and H. Haas, *Ber.*, **6**. 991, 1873;

§ 4. The Physical Properties of Molybdenum

The early preparations of molybdenum were very impure, and the description of the physical properties of these samples do not always accord with later observations. J. J. Berzelius[1] described it as a greyish-white metal; C. F. Bucholz said that it is silvery white; and L. Weiss and O. Aichel, that it is silvery white with a crystalline fracture. The hammered and drawn metal is fibrous. A. W. Hull found that the **X-radiogram** of molybdenum corresponds with a body-centred cubic lattice with sides 3·143 A. T. Fujiwara, E. C. Bain, E. Schmid, A. E. van Arkel, P. Stoll, W. P. Davey, W. Hume-Rothery, and K. Weissenberg made observations on this subject. J. Hengstenberg and H. Mark studied the effect of mechanical work on the X-radiogram; and S. T. Konobejevsky, and M. Ettisch and co-workers, the structure of hard-drawn wires. They found that the crystallites are regularly arranged, whereas in soft wires the crystallites are irregularly arranged. Z. Jeffries and R. S. Archer gave 900° for the lowest temp. of recrystallization. T. Fujiwara found that the arrangement of the fibrous structure of a hard-drawn molybdenum wire with respect to the axis of the wire is retained after bending.

For the powdered metal the older workers found values approximating 8·6 for

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H. Biltz and R. Gärtner, *ib.*, **39**. 3370, 1906; O. von der Pfordten, *ib.*, **17**. 731, 1884; A. Stavenhagen, *ib.*, **32**. 3065, 1899; A. Stavenhagen and E. Schuchard, *ib.*, **35**. 909, 1902; M. Junot, *L'Inst.*, **21**. 97, 1853; A. Vandenberghe, *Bull. Acad. Belg.*, (3), **30**. 327, 1895; *Zeit. anorg. Chem.*, **10**. 47, 1895; **11**. 385, 1896; A. Rosenheim and H. J. Braun, *ib.*, **46**. 311, 1905; W. Prandtl and B. Bleyer, *ib.*, **46**. 223, 1909; H. N. Warren, *Chem. News*, **70**. 102, 1894; C. G. Fink, *ib.*, **104**. 34, 1910; *Trans. Amer. Electrochem. Soc.*, **17**. 232, 1910; **22**. 499, 1912; *Chem. Eng.*, **12**. 51, 1910; *Met. Chem. Engg.*, **8**. 341, 1910; *Chem. News*, **104**. 34, 1911; A. Rogers and F. H. Mitchell, *Journ. Amer. Chem. Soc.*, **22**. 350, 1900; J. H. Müller, *ib.*, **37**. 2046, 1915; J. G. Children, *Phil. Trans.*, **105**. 363, 1815; E. D. Clarke, *Ann. Chim. Phys.*, (2), **3**. 55, 1816; *Journ. Science Arts*, **2**. 104, 1816; A. Sternberg and A. Deutsch, *German Pat.*, *D.R.P.* 69704, 1890; *Stahl Eisen*, **13**. 717, 1893; *Dingler's Journ.*, **289**. 288, 1893; J. J. Boericke, *U.S. Pat. No.* 1562201, 1924; J. E. Loughlin, *Amer. Journ. Science*, (2), **45**. 131, 1868; H. Mennicke, *Elektrochem. Zeit.*, **20**. 181, 215, 250, 271, 1913; B. Neumann, *Zeit. Elektrochem.*, **14**. 169, 1908; B. Neumann and H. Richter, *ib.*, **30**. 474, 1924; O. P. Watts and J. M. Breckenridge, *Electrochem. Ind.*, **6**. 237, 1908; J. G. Gahn, *Gilbert's Ann.*, **14**. 235, 1803; Wolfram-Lampen A.G., *German Pat.*, *D.R.P.* 237014, 1910; Ampère Gesellschaft, *ib.*, 240989, 1910; Badische Anilin- und Sodafabrik, *ib.*, 246554, 1911; W. Lederer, *Darstellung und Untersuchung reinen, geschmolzen Molybdäns*, Erlangen, 14, 1911; C. Lehmer, *Elektrisches Verschmelzen sulfidischer Erze und Hüttenprodukte unmittelbar auf Metall*, Halle a. S., 1906; L. Ott, *Elektrolyse geschmolzener Molybdate und Vanadate*, München, 23, 1911; A. E. van Arkel, *Chem. Weekbl.*, **24**. 90, 1927; A. Burger, *Reduktion durch Calcium*, Basel, 17, 1907; O. W. Brown, *Trans. Amer. Electrochem. Soc.*, **9**. 109, 1906; E. K. Jenckes, *ib.*, **51**. 387, 1927; E. W. Engle, *ib.*, **51**. 397, 1927; L. Andrieux, Paris, 1929; J. N. Pring and W. Fielding, *Journ. Chem. Soc.*, **95**. 1497, 1909; P. J. Hjelm, *Crell's Ann.*, i, 391, 1790; i, 179, 248, 266, 353, 429, 1791; ii, 59, 1791; i, 260, 1792; ii, 358, 1792; i, 238, 1794; *Svenska Akad. Handl.*, 280, 1788; C. F. Bucholz, *ib.*, **145**. 1825; *Scherer's Journ.*, **9**. 485, 1803; *Gehlen's Journ.*, **4**. 598, 1803; *Phil. Mag.*, **16**. 193, 1803; *Nicholson's Journ.*, **20**. 121, 188, 253, 1808; *Journ. Mines*, **18**. 241, 1808; A. W. Judge, *Aircraft and Automobile Mat. Constr.*, **1**. 668, 1920; E. Wedekind and O. Jochem, *Zeit. angew. Chem.*, **40**. 434, 1927; H. Kuzel and E. Wedekind, *Met. Chem. Engg.*, **12**. 260, 1914; K. Wolf, *Das elektrochemische Verhalten des Molybdäns und einiger Molybdänverbindungen*, Aachen, 1917; B. C. Lamble, *Trans. Canadian Min. Inst.*, **22**. 61, 1919; R. E. Pearson and E. N. Craig, *Canadian Pat. No.* 221041, 1922; *Brit. Pat. No.* 181837, 1921; L. St. C. Broughall, *ib.*, 320818, 1928; L. Kahlenberg and W. J. Trautmann, *Trans. Amer. Electrochem. Soc.*, **39**. 377, 1921; E. W. von Siemens and J. G. Halske, *Brit. Pat. No.* 286457, 1927; L. Andrieux, *Recherches sur l'électrolyse des oxydes métalliques dissoux dans l'anhydride borique ou dans les borates fondus*, Paris, 1929; *Ann. Chim. Phys.*, (10), **12**. 423, 1929; C. W. Blake, *Journ. Ind. Eng. Chem.*, **21**. 1002, 1929; C. Müller and W. Schubardt, *U.S. Pat. No.* 1759661, 1930.

[6] W. D. Coolidge, *Trans. Amer. Inst. Elect. Eng.*, **29**. 961, 1910; C. G. Fink, *Trans. Amer. Electrochem. Soc.*, **17**. 229, 1910; *Chem. News*, **104**. 34, 1910; *Chem. Eng.*, **12**. 51, 1910; N. L. Müller, *Fabrikation und Eigenschaften der Metalldrahtlampen*, Halle a. S., 1914; O. Ruff, *Zeit. angew. Chem.*, **25**. 1889, 1912; P. Schwarzkopf and S. Burgstaller, *U.S. Pat. No.* 1096464, 1914; H. Lohmann, *Brit. Pat. No.* 157769, 1921.

[7] T. Svedberg, *Die Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe*, Dresden, 486, 1909; *Ber.*, **39**. 1713, 1906; H. Küzel, *Austrian Pat. No.* 2573, 1906; *German Pat.*, *D.R.P.* 30900, 1905; 186980, 1909; *Brit. Pat. No.* 25864, 1906; J. Férée, *Compt. Rend.*, **122**. 733, 1896; E. Wedekind and O. Jochem, *Zeit. angew. Chem.*, **40**. 434, 1927; E. Wedekind, *Zeit. Koll.*, **2**. 289, 1908; L. Hamburger, *ib.*, **23**. 177, 1918.

the **specific gravity**—P. J. Hjelm gave 7·75 for the sp. gr.; H. Debray, 8·6; C. F. Bucholz, 8·62; and J. E. Loughlin, 8·56. Later observers found for the massive metal values approximating 10; thus, H. Moissan, and A. B. du Jassonneix observed 9·01; K. Wolf, 8·95 at 17°/4° (impure); T. Barratt and R. M. Winter, 9·933; W. Lederer, 10·2 at 17·5/4°; and C. G. Fink gave 10·02 for the hammered but not drawn metal; 10·04 for the metal drawn to a diameter of 3·75 mm.; 10·29, when drawn to a diameter of 0·25 mm.; and 10·32, when drawn to a diameter of 0·038 mm. E. Donath and J. Mayrhofer gave 11·5 for the at. vol.; and W. Lederer, 9·4. M. L. Huggins gave 1·54 A. for the **ionic radius;** L. Vegard, 1·03 A.; and H. G. Grimm, 0·72 A. The subject was studied by J. C. Slater, A. M. Berkenheim, V. M. Goldschmidt, L. Pauling, and E. T. Wherry. The results show that for sexivalent molybdenum atoms, the effective at. radius is 0·62 A., for quadrivalent atoms, 0·66 to 0·83 A., and for typical molybdenum atoms, 1·36 A. I. Traube investigated the at. soln. vol.; and P. Vinassa, the mol. number.

J. J. Berzelius said that the metal is harder than topaz; H. Moissan, and A. B. du Jassonneix, that it does not scratch glass or quartz; and J. R. Rydberg gave 8·5 for the **hardness** on Mohs' scale. E. W. Engle gave 147 for the hardness of molybdenum on Brinell's scale. According to H. Moissan, A. B. du Jassonneix, and F. Wohler, molybdenum can be filed, and, when hot, it can be forged—hammered and rolled. C. G. Fink found the **tensile strength** of wires 0·125 mm. diameter to be 140 to 180 kgrms. per sq. mm.; wires 0·07 mm. diameter, 161 to 189 kgrms. per sq. mm.; and wires 0·038 mm., 189 to 217 kgrms. per sq. mm. W. P. Sykes measured the tensile strength of molybdenum wires after different heat treatments. No. 1 was swaged and drawn hot (1000°–1300°) from a diameter of 0·125 to 0·025 in.; No. 2 was similarly treated at 800°; No. 3 was swaged and drawn hot (1000°–1300°) from 0·045 to 0·025 in.; No. 4 was similarly treated at 800°; No. 5 was annealed to give medium grain size; No. 6 was annealed to give small grain size; and No. 7, annealed to give large grain size. The tensile strengths in lbs. per sq. in. are shown in Fig. 2; the percentage elongation per 2 in., in Fig. 3; and the percentage reduction in area, in Fig. 4. These observations were discussed by Z. Jeffries and R. S. Archer. P. Ludwik studied the effect of temp. T. Fujiwara found that the tensile strength of molybdenum is 20 per cent. greater when the tension is applied in a direction parallel to that of rolling than it is when the tension is applied at an angle of 45° or 90° to the direction of rolling:

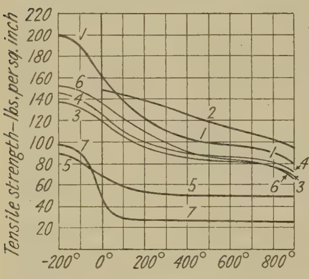


Fig. 2.—Tensile Strength of Molybdenum.

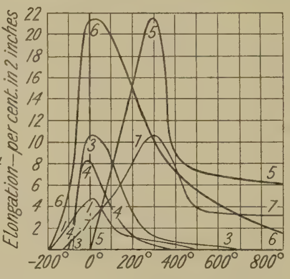


Fig. 3.—Elongation of Molybdenum.

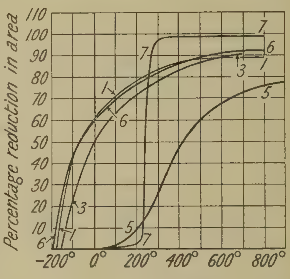


Fig. 4.—Reduction of Area of Molybdenum.

Direction of rolling	0°	22·5°	45°	67·5°	90°
Tensile strength	113·9	101·2	94·8	97·0	92·8 kgrms. per sq. mm.

J. Königsberger gave 250 to 270 kgrms. per sq. mm. for the tensile strength of molybdenum wires, and 125 kgrms. per sq. mm. for single crystal wires. The **torsion modulus** was found to be $13{\cdot}5\times10^{11}$ to 15×10^{11} C.G.S. units; and for single crystal wires, 18×10^{11} C.G.S. units. A. L. Kimball and D. E. Lovell found the **elastic modulus,** E, of swaged molybdenum to be $34{\cdot}6\times10^{11}$ dynes per sq. cm.

They also measured the internal friction. W. Widder gave $E=E_{20}\{1-0\cdot0004032(\theta-20)\}$. E. Edwards and co-workers examined the increase in torsional stiffness produced by increasing the tension of molybdenum wires. G. Grube and F. Lieberwirth, and J. Laissus studied the **diffusion** of molybdenum into iron. According to T. W. Richards and E. P. Bartlett, the **compressibility** is $0\cdot47\times10^{-6}$ at 20° for one megabar at 20°, at press. between 100 and 500 megabars. P. W. Bridgman found the compressibility, β, of swaged rod at 30° to be $\delta v/v=-10^{-7}(3\cdot47-1\cdot2p)p$, and at 75°, $-10^{-7}(3\cdot48-1\cdot2p)p$; and for drawn wire at 30°, $\delta v/v=-10^{-7}(3\cdot61-1\cdot0p)p$, and at 75°, $-10^{-7}(3\cdot62-1\cdot0p)p$, for p kgrms. per sq. cm. with p between 1 and 12,000. For drawn wire and swaged rod respectively at 30°, $\beta=0\cdot0_6361$ and $0\cdot0_6347$; $\delta\beta/\beta\delta p=0\cdot0_558$ and $0\cdot0_572$; $-\delta\alpha/\alpha\delta p=0\cdot0_52$ and $0\cdot0_52$; and $\beta_0-1(\delta\alpha/\alpha\delta p)=5\cdot54$ and $5\cdot76$, where α denotes the coeff. of thermal expansion. L. H. Adams gave $\delta\beta=-0\cdot02$. P. W. Bridgman studied the effect of pressure on the rigidity.

C. G. Fink found $\alpha=0\cdot0_536$ for the coeff. of **thermal expansion** between 20° and 100°, and B. Beckman, $\alpha=0\cdot0_556$. The thermal expansion of an exceptionally pure sample of molybdenum was found by L. W. Schad and P. Hidnert to be represented by the expression : Length at $\theta°$, $l=l_0(1+5\cdot15\theta\times10^{-6}+0\cdot00570\theta^2\times10^{-6})$ for $\theta°$ between $-142°$ and 19° ; and between 19° and 305°, length at $\theta°$ is $l=l_0(1+5\cdot01\theta\times10^{-6}+0\cdot00138\theta^2\times10^{-6})$ with a probable error less than 3×10^{-6} per unit length. P. Hidnert and W. B. Cero gave for the mean coeff. of linear expansion, $\alpha=0\cdot0_549$ between 25° and 100° ; and $0\cdot0_555$ between 25° and 500°. If l_0 denotes the length at 300° K., and l, the length at $T°$ K., W. Widder gave $0\cdot0_5549$ at 20° and $0\cdot0_5416$ at 190° for the coeff. of thermal expansion. A. G. Worthing represented the measurements by $l/l_2=0\cdot0_2500(T-300)+0\cdot0_8105(T-300)^2$. C. Zwikker found for the linear expansion l/l_0, 1·00623 at 1440° ; 1·00760 at 1648° ; 1·00920 at 1855° ; and 1·0111 at 2059°. According to E. Podszus, wires of molybdenum or of molybdenum-tungsten alloy may be sealed gas-tight into vitreous quartz by the aid of the flux : silica 10, alumina 1, boric oxide 1, and orthoclase 2. J. Disch gave for the expansion of molybdenum wires in mm. per litre between 0° and $\theta°$:

	−190°	−78°	0·00°	100°	200°	300°	400°
Expansion .	−0·79	−0·375	0·00	0·52	1·07	1·64	2·24 mm.

T. Barratt and R. M. Winter gave for the **thermal conductivity** of molybdenum 0·346 cal. per sec. per degree at 17°, and 0·333 cal. at 100°. C. Zwikker gave for the thermal conductivity k in watts per cm. per degree :

	1234°	1440°	1648°	1855°	2059°	2259°	2460°
k . .	0·98	1·00	1·02	1·05	1·11	1·17	1·24

J. Dewar gave 0·0141 for the **specific heat** between $-253°$ and $-196°$, and 1·35 for the **atomic heat ;** P. Nordmeyer obtained too high a value 0·062 between $-188°$ and 20°, for T. W. Richards and F. G. Jackson obtained 0·0555 for the sp. ht. and 5·33 for the at. ht. ; A. de la Rive and F. Marcet obtained respectively 0·0659, and 6·33 between 5° and 15° ; H. V. Regnault, respectively 0·0722 and 6·93 between 0° and 100° ; W. Lederer obtained the unlikely value 0·0461 between 17° and 100° ; whilst for a metal with only 0·22 per cent. impurity, E. Defacqz and M. Guichard obtained respectively 0·0723 and 6·94 between 15° and 91° ; 0·0735 and 7·06 between 15° and 264° ; and 0·0740 and 7·10 between 15° and 440° ; N. Stücker, 0·0647 and 6·21 between 20° and 100°, and 0·0722 and 6·93 between 20° and 550° ; and P. Nordmeyer and A. L. Bernoulli, 0·063 between 0° and $-185°$; N. Stücker gave for the true sp. ht.

	60°	125°	225°	325°	425°	525°
c . .	0·06468	0·07076	0·06912	0·06967	0·08206	0·08121

$c=0\cdot0708-0\cdot000052(\theta-125)+0\cdot0_64(\theta-125)^2$, between 125° and 225° ; $c=0\cdot0707-0\cdot000027(\theta-125)+0\cdot0_61(\theta-125)^2$, between 125° and 325° ; $c=0\cdot0697-0\cdot000113(\theta-325)+0\cdot0_61(\theta-325)^2$, between 325° and 425° ; $c=0\cdot0697+0\cdot000190(\theta-325)-0\cdot0_67(\theta-325)^2$, between 325° and 525 ; $c=0\cdot0708$

$-0·000037(\theta-125)^{\circ}-0·0_{6}3(\theta-125)$, between 125° and 525°; and $c=0·0647+0·000094(\theta-60)$, between 60° and 125°. T. E. Stern gave $c=0·06054$ between 0° and 108°; 0·06333 between 0° and 441·5°; and $C_p=0·05973+0·00001619\theta$, at temp. θ between 0° and 441·5°. D. Cooper and G. O. Langstroth gave:

	—40°	0°	25°	50°	100°	150°	200°	250°
Sp. ht. .	0·0564	0·0589	0·0597	0·0609	0·0612	0·0616	0·0624	0·0632

and the results are plotted in Fig. 5; the at. ht. was represented by $C_v=0·0593+0·0_{4}13(\theta+40)-0·0265(\theta+40)^{-1·06}$. F. Wüst and co-workers found $C_p=6·11$ at 100°, and 7·80 at 900°. H. A. Jones gave $c=0·0578+0·0000257T$; and C. C. van Voorhis, $c=0·0606+0·000028T$. F. Simon and W. Zeidler gave $C_p=D(379T-1)+0·0_{4}263T^{\frac{3}{2}}$; and for C_v between 16° K. and 24° K., $C_v=0·0785T^3$; they also gave the following values for at. ht. of molybdenum:

T° K. .	15·97°	20·66°	31·52°	56·0°	105·6°	144·6°	200·2°	274·7°
C_p .	0·040	0·073	0·264	1·230	3·380	4·38	5·09	5·53
C_v .	0·040	0·073	0·264	1·230	3·374	4·37	5·06	5·49

H. A. Jones and co-workers gave $C_p=4·88+0·00248T$. J. Maydel discussed some relations of the sp. ht.; and E. D. Eastman and co-workers, the thermal energy of the electrons in molybdenum, and computed $C_p-C_v=0·047$ Cal. per degree per mol.

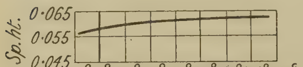


FIG. 5.—The Effect of Temperature on the Specific Heat of Molybdenum.

R. C. Smith gave 800° for the sintering temp. of molybdenum filings. According to H. von Wartenberg, the **melting point** of pure molybdenum is 2550° when that of platinum is 1745°. C. W. Waidner and G. K. Burgess, and W. R. Mott gave 2500°; M. Pirani, 2450°; M. von Pirani and A. R. Meyer, 2450°; A. G. Worthing, 2622°±10°; E. Siedschlag, 2530°; and M. von Pirani and H. Alterthum, 2840°±40°. For a commercial sample, O. Ruff and O. Goecke gave 2110°. H. Moissan distilled the metal in an electric arc furnace; and W. R. Mott estimated the **boiling point** of the metal to be 4700°; I. Langmuir calculated 3617°. C. Zwikker gave 4780° K. for the sublimation temp. at 1 atm. press. I. Langmuir measured the **rate of evaporation** from hot filaments, and W. H. Rodebush observed the value of A in the equation for the number of electrons evaporating from a metal filament, $n=AT^{-\frac{1}{2}}e^{-b/T}$ per sq. cm. per second, to be $1·32\times10^{26}$; the calculated result at 2000° K. is $5·50\times10^{26}$. I. Langmuir represented the rate of evaporation m grms. per sq. cm. per sec. to be $\log m=17·11-38600T^{-1}-1·76\log T$, or

T° K. . .	1994°	2040°	2121°	2287°	2326°	2373°
$m\times10^6$ . .	0·00766	0·0305	0·124	1·74	3·65	8·47

and C. Zwikker, $\log m=-33800T^{-1}+8·24$ grms. per sq. cm. per sec. The subject was discussed by F. J. Wilkins, and H. A. Jones and co-workers. For the **vapour pressure,** p mm., I. Langmuir gave $\log p=17·354-38600T^{-1}-1·26\log T$, or

T° K. . .	1800°	2000°	2500°	2800°	3890°
p	$6·43\times10^{-9}$	789×10^{-9}	$43·0\times10^{-9}$	1679×10^{-9}	760

C. Zwikker gave $\log p=33800T^{-1}+10·16$ mm.; and J. A. M. van Liempt, $\log p=-37710T^{-1}+9·90$, and 43·53 to 44·96 for **Trouton's constant.** W. Herz estimated that the **heat of fusion** lies between 1000 and 5000 cals. I. Langmuir gave for the latent **heat of vaporization** $177,000-2·5T$; and for the **chemical constant,** 4·4. W. Zeidler gave 170,400 cals. for the heat of vaporization, and 4·07 for the chemical constant. G. N. Lewis and co-workers, and E. D. Eastman gave 7·5 for the at. **entropy** of molybdenum at 25°; W. Herz, 12·66; R. C. Tolman, 56·4 at 25°; and B. Bruzs, 23·0 at the m.p. R. D. Kleeman discussed the internal energy of molybdenum; and W. Herz, the entropy. M. Delépine gave for the **heat**

of oxidation, $\mathrm{Mo+3O=MoO_3}$+166·14 Cals. at constant vol., and 167 Cals. at constant press. W. Lederer gave 168·576 Cals.; J. E. Moose and S. W. Parr, 1829 Cals. per gram; and W. G. Mixter, 181·5 Cals. for the oxidation of the metal by sodium dioxide.

W. W. Coblentz [2] observed the percentage **reflecting power,** R, for light of wave-length λ to be:

λ .	0·40	0·7	1·0	1·4	2·0	4·0	6·0	1·0	1·2
μ .	44·0	49·8	58·2	69·0	81·6	90·5	93·0	94·5	95·2

G. Jaffé calculated theoretical values for these constants. W. W. Coblentz said that the reflectivity curves of molybdenum and tungsten are so nearly alike that from a consideration of their emissivities and luminous efficiencies there seems to be no great choice in the use of these two metals in incandescent lamps. On the other hand, from a consideration of their physical properties, the molybdenum filament would be preferable because of its toughness and its ductibility, in contrast with tungsten which is very brittle. Their m.p. are high, and it is principally a question of overcoming certain physical weaknesses in the molybdenum in order to make it practical. A. G. Worthing gave for the spectral emissivity, e, of molybdenum for wave-lengths 0·665μ and 0·475μ, from 273° K. to the m.p., 2895° K.; for the average visible emissivity, e_v; the colour emissivity, e_c; and the total emissivity, e_t,

T° K. .	273°	400°	800°	1200°	1600°	2000°	2400°	2895°
e { 0·665μ.	0·420	0·415	0·398	0·390	0·367	0·353	0·341	0·328
e { 0·475μ.	0·425	0·421	0·409	0·403	0·388	0·279	0·371	0·363
e_v . .	—	—	—	0·393	0·373	0·362	0·352	0·342
e_c . .	—	—	—	0·361	0·321	0·297	0·277	0·255
e_t . .	—	—	—	0·096	0·168	0·210	0·248	0·290

The values for the spectral emissivity at room temp. for 0·665μ and 0·475μ, are respectively 0·580 and 0·576. The subject was studied by C. Zwikker, C. Davisson and L. H. Germer, R. L. Petry, E. Patai, and S. Dushman and co-workers—*vide* tungsten. A. G. Worthing found for the brightness temp., T_b for wave-lengths 0·665μ; the colour temp., T_c; and the radiation temp., T_v:

T° K. . .	1000°	1400°	1800°	2200°	2600°	2895°
T_b . .	958°	1316°	1658°	1986°	2297°	2519°
T_c . .	1004°	1411°	1823°	2244°	2672°	2997°
T_v . .	557°	864°	1187°	1523°	1866°	2122°

The normal brightness, B candles per sq. cm.; the radiation intensity, η watts per sq. cm.; and the luminous efficiency in lumens per watt, are:

T° K. . .	1000°	1400°	1800°	2200°	2600°	2895°
B . .	0·00010	0·089	4·13	48·5	270	730
η . .	0·55	3·18	11·3	30·7	69·5	116
Efficiency .	—	0·093	1·22	5·28	13·0	—

E. S. Lamar and W. E. Deming studied the distribution of temp. in a heated filament. S. C. Roy, M. J. Martin, and A. T. Watermann studied the variation of the thermionic emission with temp.; A. W. Hull and J. M. Hyatt, J. M. Hyatt and H. A. Smith, E. Meyer, and H. B. Wahlin, the secondary emission of electrons; W. J. Jackson, the emission of electrons by bombardment with positive ions; R. L. Petry, the critical potential for the emission of secondary electrons; E. Meyer and L. P. Smith, the emission of positive ions; T. Soller, and L. J. Haworth, the velocity of the secondary electrons; H. R. Kiehl and co-workers, W. R. Ham and M. W. White, the emission of electrons from a molybdenum target; and the radiation, by A. L. Helfgott; the reflection of electrons from molybdenum was studied by W. R. Ham; the diffraction of electrons, by E. Rupp; the liberation of electrons by positive ions, by M. L. E. Oliphant; and the heat of condensation of electrons and positive ions on molybdenum, by C. C. van Voorhis and K. T. Compton. The cold electronic discharge from molybdenum was investigated by R. J. Piersol; the heats of condensation of electrons and positive ions, by C. C. van Voorhis; the photoelectric effect, by H. Klumb; the electron theory of thermionic emission, by R. H. Fowler; electronic collisions, by M. Pirani and H. Schönborn.

R. Bunsen,[3] G. Merz, and C. F. Plattner discussed the flame reactions of molybdenum compounds. The colourless blowpipe flame is coloured greenish-yellow. R. T. Simmler found that molybdic oxide, in the colourless gas flame, gives a continuous **flame spectrum.** W. N. Hartley and H. Ramage studied the banded spectrum in the oxy-hydrogen flame. The **spark spectrum** was investigated by W. A. Miller, R. Thalén, J. N. Lockyer, E. Demarçay, F. Exner and E. Haschek, M. Eppley, C. Weigand, M. A. Catalan, E. O. Hulburt, R. J. Lang, H. Nagaoka and co-workers, O. Lohse, A. Hagenbach and H. Konen, A. G. G. Leonard, and J. Formanek. The principal lines are 6030, 5888, and 5857 in the orange-yellow; 5792 and 5751 in the yellow; 5688 in the yellowish-green; 5570, 5532, and 5506 in the green; and 4278 in the indigo-blue. E. O. Hulburt studied the spectrum of the condensed spark in soln. of the salts; and E. J. Allin and H. J. C. Ireton, the under-water spark-spectrum. The **arc spectrum** was studied by B. Hasselberg, F. Croze, M. Eppley, M. Puhlmann, C. Weigand, M. A. Catalan, C. C. Kiess and W. F. Meggers, and F. Exner and E. Haschek; the **ultra-violet spectrum,** by W. A. Miller, J. C. McLennan and A. C. Lewis, R. J. Lang, T. Aden, and F. Exner and E. Haschek. According to W. H. Fulweiler and J. Barnes, the light of the molybdenum arc, under water, gives a continuous spectrum in the ultra-violet. The **ultra-red spectrum** was studied by J. M. Eder and E. Valenta. The effect of *pressure* was examined by W. J. Humphreys; and of a *magnetic field*, or the **Zeeman effect,** by R. Jack, E. Wilhelmy, and M. A. Catalan. J. N. Lockyer studied the *enhanced lines*; H. Geisler, the *anomalous dispersion* of light in the vapour of molybdenum; and M. Kimura and G. Nakamura, *enhanced lines*. No **series spectrum** has been observed, but E. Paulson noted some pairs of constant difference lines; P. G. Nutting, O. Laporte, and M. A. Catalan have studied the *structure of the line spectrum.* Unlike J. E. Paulson, M. Puhlmann observed no lines in the arc spectrum which exhibit constant frequency differences. The subject was discussed by M. A. Catalan. C. C. Kiess, W. F. Meggers and C. C. Kiess, R. C. Gibbs and H. E. White, and C. C. Kiess and O. Laporte studied the series spectrum. F. Croze studied the ultimate rays and resonance rays of molybdenum.

H. B. Dorgels studied the **absorption spectrum** of the vapour. According to J. Formanek, although colourless aq. soln. of molybdenum salts give no characteristic absorption spectrum, a soln. of the chloride in absolute alcohol gives a green soln. which if concentrated shows absorption bands in the red, blue, and violet, but no lines. If about two drops of tincture of alkanna be added to the soln. of molybdenum chloride, in absolute alcohol, the brownish-red soln. has narrow bands at 6002, 5560, and 5185, and a band in the violet. The soln. however, gradually becomes violet, then blue with a reddish fluorescence; and the narrow bands are displaced to the right until finally in about 10 hrs., when equilibrium is attained, the narrow bands occur at 5845, 6415, and 5040. The spectrum is not changed by the addition of a little ammonia, but an excess makes the liquid turbid and the spectral bands move to the left. C. Horner studied the spectra of beads of boric or phosphoric acid containing molybdenum oxide in soln. S. Kato studied the absorption spectrum of aq. soln.

The K-series in the **X-ray spectrum** was measured by F. C. Blake and W. Duane,[4] S. Tanaka and J. Tsutsumi, L. H. Martin, J. W. M. du Mond, F. L. Nutting, J. Valasek, H. Mark and G. von Susich, F. Wisshak, D. Mitchell and B. Davis, N. S. Gingrich, B. Davis and co-workers, L. R. G. Treloar, A. P. R. Wadlund, J. Schrör, H. Purks, B. Davis and H. Purks, Y. H. Woo, B. Walter, A. Dauvillier, S. Björek, D. Nasledoff and P. Scharawsky, M. Siegbahn, H. R. Robinson and co-workers, A. Larsson, A. Jönsson, A. Liede, D. Coster and co-workers, P. A. Ross, E. O. Wollan, F. K. Richtmyer, F. K. Richtmyer and L. S. Taylor, M. Balderston,

F. K. Richtmyer and R. C. Spencer, H. A. Erickson, A. Bouwers, G. E. M. Jauncey and A. H. Compton, A. H. Compton, G. Kettmann, P. Anger, A. H. Compton and Y. H. Woo, S. K. Allison and co-workers, G. E. M. Jauncey, M. Siegbahn and E. Friman, M. de Broglie, A. P. R. Wadlund, S. Tanaka and J. Tsutsumi, H. G. J. Moseley, and J. Malmer. The lines include $\alpha_2\alpha'=0{\cdot}71196$; $\alpha_1\alpha=0{\cdot}759$; $\beta_1\beta=0{\cdot}63065$; and $\beta_2\gamma=0{\cdot}61398$. The L-series was measured by D. Coster, E. Hjalmar, M. Siegbahn and A. Larsson, H. G. J. Moseley, J. Malmer, F. K. and R. D. Richtmyer, M. Siegbahn and E. Friman, W. Bothe and H. Franz, S. Björek, W. Bothe, M. J. Druyvesteyn, W. Duane and R. A. Paterson, H. Hirata, B. B. Ray, A. Jönsson, A. H. Compton and R. L. Doan, J. Zahradnicek, J. M. Cork, H. R. Robinson and C. L. Young, and M. Siegbahn. The lines include $\alpha_2\alpha^1=5{\cdot}400$; $\alpha_1\alpha=5{\cdot}3943$; $\alpha_3\alpha^{11}=5{\cdot}3721$; $\beta_1\beta=5{\cdot}1658$; and $\gamma_1\delta=4{\cdot}7111$. A. Dauvillier observed no $M\alpha$-ray ; but J. Thibaud found the $M\alpha$-line=65·0 A. O. W. Richardson and C. B. Bozzani, and C. B. Bozzani and C. T. Chu found that the critical potential of the X-ray radiation from a tungsten wire is 356 volts corresponding with a wave-length of 34·8 A. The calculated $M\alpha$-line of molybdenum is 35·2 A., indicating that the observed radiation is the M-series. The M-series was also studied by S. Björek, H. R. Robinson and C. L. Young, and J. M. Cork ; and the N-series by S. Björek, and H. R. Robinson and C. L. Young. E. O. Wollan found that the $K\alpha$-lines are not polarized more than one per cent. W. Ehrenberg and co-workers studied the widths of the X-ray emission lines.

J. E. P. Wagstaff gave $6{\cdot}7\times10^{12}$ for the **vibration frequency.** F. Wagner discussed the linear relation between the at. numbers and the frequency. According to T. E. Auren, the at. absorption coefficient for X-rays is 244 when that of hydrogen is unity. R. A. Houstoun, P. Günther, L. M. Alexander, K. A. Wingärdh, and F. W. Warburton and F. K. Richtmyer also studied this subject. S. K. Allison and W. Duane, G. Hagen, F. Kirchner, E. N. Coade, R. W. G. Wyckoff, and G. L. Clark and co-workers studied the scattering of the X-rays from molybdenum, and the Compton effect ; J. Hengstenberg, the reflection of X-rays ; H. R. Robinson and co-workers, and R. Whiddington, the emission from molybdenum bombarded by X-rays ; G. L. Clark and co-workers, the action of primary X-rays from a molybdenum target on the secondary and tertiary rays from various substances. M. A. Rewutzka, and O. W. Richardson and F. S. Robertson investigated the soft X-rays from molybdenum ; L. P. Davis, the effect of oxidation on the emission of soft X-rays ; and G. B. Bandopadhyaya, and O. W. Richardson and F. S. Robertson, the photoelectric effect of these rays. R. Whiddington, studied the velocity of the electrons liberated by X-rays from molybdenum ; D. Nasledoff and P. Sharawsky, D. L. Webster and A. E. Hennings, A. Jönsson, and A. Bouwers, the velocity of the X-rays ; and C. C. van Voorhis and K. T. Compton, the heat of condensation of electrons. M. A. Catalan gave for the **ionization potential,** 7·1 volts ; and the first **resonance potential,** 3·19 volts. L. Rolla and G. Piccardi studied the electronic equilibrium and ionizing potentials of molybdenum, etc. D. L. Webster and A. E. Hennings studied the penetration by cathode rays ; H. R. Robinson, the secondary corpuscular X-rays ; W. Herz gave $7{\cdot}27\times10^{6}$ for the **vibration frequency.**

M. J. Martin [5] found that photoelectric currents are produced by the action of the light from a quartz mercury lamp on molybdenum heated in vacuo to 1325°. The sensitiveness of the **photoelectric effect** increases to a final limiting value, and the wave-length limit shifts from about 2600 A. to 3800 A. The work function is 3·22 volts. The subject was studied by T. Pavolini. N. Piltschikoff observed that molybdenum emits practically no **Moser rays.** J. Lifschitz, and R. T. Dufford investigated the **volta-luminescence** which occurs with an electrolytic cell under certain conditions when molybdenum electrodes are used.

K. F. Herzfeld [6] discussed the metallic conductivity of molybdenum. According to C. G. Fink, the **electrical resistance** of hard-drawn molybdenum wire is $5{\cdot}6\times10^{-6}$ ohm per cm. cube, and of annealed wire, $4{\cdot}8\times10^{-6}$ ohm at 25°. The temp. coeff. is

0·5 per cent. per degree between 0° and 170°. C. E. Blom gave $R \times 10^{-4} = 22{\cdot}4$ ohms for the resistance of molybdenum at 0°, and at θ°, $R \times 10^{7} = 44 \times 0{\cdot}117\theta + 0{\cdot}00053\theta^2$ ohms per cm. cube. A. Schulze gave $R = R_0(1 + 0{\cdot}004020\theta + 0{\cdot}0512\theta^2)$. C. Zwikker found for the sp. resistance in microhms per cm.:

	1234°	1440°	1648°	1855°	2059°	2259°	2460°
R . .	29·2	35·2	41·2	47·3	53·5	59·7	66·0

A. A. Sommerville found that the effect of temp. is very sensitive to the degree of purity of the metal, and he gave 0·0034 for the temp. coeff. of the resistance, whilst P. W. Bridgman gave 0·004336 between 0° and 100°. A. A. Somerville represented his results for the effect of temp. on the resistance, and on the temp. coeff. of the resistance by the curves, Fig. 6. W. Geiss and J. A. M. van Liempt gave for the resistance of single crystals 0·0502 ohm per metre for wire 1 mm. cross-section, and the temp. coeff. was 473×10^{-5}. A. G. Worthing gave for the resistance, R milliohms, and for the temp. coeff.,

T° K. .	273°	400°	1000°	1400°	1600°	2000°	2400°	2600°	2895°
R .	5·14	8·15	23·9	35·2	41·1	53·1	65·5	71·8	81·4
a .	1·265	1·170	1·145	1·145	1·145	1·145	1·145	1·145	1·145

L. Holborn gave for wire annealed at 500° the ratio of the resistance, R, at θ° to that, R_0, at 0°:

	−192°	−78°	100°	200°	300°	400°
R/R_0 . .	0·193	0·667	1·435	1·885	2·349	2·825

and for the temp. coeff., a, of the resistance:

	−135°	−39°	50°	150°	250°	350°
a .	0·00415	0·00427	0·00435	0·00450	0·00464	0·00478

W. Geiss and J. A. M. van Liempt studied the effect of temp. on the resistance; and J. C. McLennan and co-workers, the effect of temp. in the vicinity of 2·2° K.; L. Holborn gave 0·00435 for the temp. coeff.; P. Kapitza, the influence of a magnetic field on the conductivity. Z. A. Epstein compared the conductivities of the elements and their position in the periodic table. A. T. Waterman discussed the electronic theory of conduction. W. Geiss and J. A. M. van Liempt found that the product of the sp. resistance and the temp. coeff. is constant in agreement with Matthiessen's rule. H. Rolnick found that the resistance decreases with tension. U. Fischer, and B. Beckman measured the influence of pressure, p kgrms. per sq. cm., on the resistance; and P. W. Bridgman found the relative resistance and the press. coeff. to be:

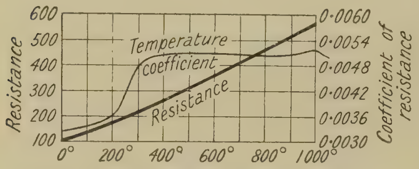


FIG. 6.—The Effect of Temperature on the Resistance of Molybdenum.

		0°	25°	50°	75°	100°
R		1·0000	1·1071	1·2150	1·3238	1·4336
Press. coeff.	0 kgrm. .	$-0{\cdot}0_5133$	$-0{\cdot}0_5132$	$-0{\cdot}0_5131$	$-0{\cdot}0_51305$	$-0{\cdot}0_5130$
	12,000 kgrms .	$-0{\cdot}0_51245$	$-0{\cdot}0_5124$	$-0{\cdot}0_5124$	$-0{\cdot}0_51235$	$-0{\cdot}0_5123$
	average . .	$-0{\cdot}0_51286$	$-0{\cdot}0_51281$	$-0{\cdot}0_51275$	$-0{\cdot}0_51270$	$-0{\cdot}0_51265$

U. Fischer gave

	13·2°	0·1°	−75°	−192°	−252·7°
Coeff. . . .	$0{\cdot}0_5134$	$0{\cdot}0_5135$	$0{\cdot}0_5150$	$0{\cdot}0_5269$	$0{\cdot}0_5414$ to $0{\cdot}0_549$

S. Morugina found that the molybdenum-tungsten thermocouple had an e.m.f. which changes sign at about 1900°. The e.m.f. are small being about −3 millivolts at 1000°; and +1·5 at 2000°, so that the couple is of little practical value. W. Rohn studied the thermoelectric force of molybdenum against nickel.

P. W. Bridgman found the **thermolectric force,** in volts ×106, of the metal uncompressed and compressed to p kgrms. per sq. cm. to be:

p	10°	20°	40°	60°	80°	100°
2,000 . .	0·012	0·025	0·065	0·109	0·129	0·140
6,000 . .	0·037	0·078	0·209	0·328	0·383	0·415
10,000 . .	0·057	0·125	0·357	0·543	0·634	0·693
12,000 . .	0·066	0·146	0·430	0·649	0·761	0·833

for **Peltier's effect** in joules per coulomb $\times 10^6$ between the uncompressed and compressed metal:

p	0°	20°	40°	60°	80°	100°
2,000 . .	0·30	0·38	0·53	0·47	0·25	0·15
6,000 . .	0·95	1·35	2·41	1·23	0·74	0·48
10,000 . .	1·45	2·28	4·23	2·00	1·23	0·93
12,000 . .	1·69	2·93	4·83	2·44	1·52	1·16

and for **Thomson's effect** in joules per coulomb per °C. $\times 10^6$ expressed as the excess with the compressed over the uncompressed metal:

p	0°	20°	40°	60°	80°	100°
2,000 . .	0	0·6	0·3	−1·3	−1·1	0·0
6,000 . .	0·8	4·4	−2·5	−7·0	−1·8	−1·1
10,000 . .	1·2	13·2	−9·4	−9·3	−2·5	−1·9
12,000 . .	1·6	15·2	−11·6	−9·7	−3·2	−2·2

The thermoelectric force against lead is given by $(5{\cdot}892\theta+0{\cdot}02167\theta^2-0{\cdot}000025\theta^3)\times10^{-6}$ volts; the Peltier's effect, by $(5{\cdot}892+0{\cdot}04334\theta-0{\cdot}000075\theta^2)(\theta+273)\times10^{-6}$ volts; and the Thomson's effect by $(0{\cdot}04334-0{\cdot}0001500\theta)(\theta+273)\times10^{-6}$ volts per °C. C. Zwikker found that the Thomson's effect of molybdenum is negligibly small at about 2000° K., being less than —2 millivolts per degree. E. Blumenthal measured the thermoelectric force of molybdenum against tungsten, and also against tantalum.

R. D. Kleeman and W. Frederickson found that molybdenum wire through which an electric current is passing, acquires a negative charge. M. Forro and E. Patai found the contact potential of sodium against molybdenum to be 2·0 volts; and they measured the contact potential of molybdenum and mercury. E. Dubois studied the Volta effect in water vapour. A. S. Russell and S. W. Rowell said that the position of molybdenum in the electrochemical series is approximately the same as that of mercury. This was determined by finding the most noble metal that can displace them from soln., and the order, relative to metals of known potential, in which it is removed from mercury by oxidation with permanganate. According to L. Marino, although molybdenum can act as a bi-, ter-, or sexivalent element, electrochemically, it acts only as a hexad. It can occur under widely varying conditions in the active and **passive states,** each of which corresponds with its own specific e.m.f. Between these two states, there is an indefinitely large number of other states corresponding with the varying conditions of the surface of the metal. W. Muthmann and F. Fraunberger found that the highest numerical values of the e.m.f. in the two states in N-KCl were —0·74 volt (active) and +0·66 volt (passive). Two fresh pieces had the air potentials 0·26 and —0·02 volt. H. Kuessner observed that two different pieces of metal—containing traces of carbon, and of oxide, and a little iron—behaved differently. One became passive when the current density was about 0·05 amp. per sq. cm., whilst the other showed no signs of passivity even with larger current densities. L. Marino showed that the metal is active when in contact with strongly oxidizing soln., such as those of chlorine, bromine, nitric acid, or chloric acid, at the ordinary temp.; further, it is active in soln. of highly oxygenated salts, but only at temp. rising with the dilution, and also in conc. soln. of certain other acids only capable of dissolving it at their b.p., the e.m.f. being here identical with that exhibited in soln. able to dissolve it readily. W. Muthmann and F. Fraunberger found that the initial and end potentials with 40 per cent. nitric acid were respectively —0·22 and 0·38 volt; with conc. chromic acid, —0·72 and 0·66 volt; with

20 per cent. hydrochloric acid, —0·06 and 0·29 volt; with 16 per cent. sulphuric acid, 0·02 and 0·26 volt; with ammonium persulphate, —0·48 and 0·45; and with 10 per cent. ferric chloride, —0·27 and 0·48 volt. According to L. Marino, the inactive condition of the metal is only possible for certain values of the current density, a fact which indicates the great influence of the latter magnitude on the surface of the metal. This influence is shown most distinctly in soln. of substances rich in oxygen, such as nitric acid and nitrates. Neglecting the slight influences exerted by different electrolytes, the highest value of the e.m.f. after the metal has acted for some seconds as a cathode is 1·50 volts for the active condition and 0·20 volt for the passive condition. The inactive state of the metal is unstable, and, as soon as its cause is removed, reverts to the active condition, the change proceeding more rapidly than with chromium. W. Muthmann and F. Fraunberger observed that bases and reducing agents activate the passive metal. Thus, the initial and end potentials with a conc. soln. of potassium hydroxide were respectively 0·13 and —0·72 volt; with aq. ammonia, 0·29 and —0·31; and with alkaline formaldehyde, 0·33 and —0·31 volt. Active molybdenum reduces soln. of mercuric, cupric, and ferric salts as well as salts of silver, gold, and platinum. L. C. Bannister and U. R. Evans measured the time-potential curves. G. C. Schmidt made observations on this subject. R. Lorenz reported the **electrode potential** of powdered molybdenum in 0·1N-molybdatosulphuric acid to be 0·41 volt; and K. Wolf, from measurements of the potential in alcoholic soln. of molybdenum dichloride calculated 0·53 to 0·55 for the normal electrode potential—but the numbers have little practical value owing to the quick changes which occur in the e.m.f. of cells. Thus L. Marino measured the e.m.f. of the cell, Mo | MX | KCl,HgCl | Hg, where MX represents a neutral salt, acid, or base, and of the cell, Mo | MX | H_2CrO_4 | Pt. The highest value with active molybdenum was 1·5 volt, and with passive molybdenum 0·2 volt—the difference 1·3 volt, and W. Muthmann and F. Fraunberger observed the difference to be 1·4 volt. All cells with a molybdenum electrode showed great difference in their e.m.f. owing to the passivation of the metal. O. Bauer gave —0·200 volt in one per cent. sodium chloride at the start, and —0·164 after 120 hrs. A. Thiel and W. Hammerschmidt found the **overvoltage** with 2N-H_2SO_4 is 0·168 volt at 25°. S. J. French and L. Kahlenberg, and A. C. Krüger and L. Kahlenberg studied the gas-metal electrodes of molybdenum and oxygen, nitrogen, or hydrogen. A. S. Russell and S. W. Rowell found that molybdenum and tungsten are in some respects more reactive than copper but in other respects they resemble mercury, and silver. The values for the electrode potentials are not concordant. O. Collenberg studied the oxidation potential of potassium molybdenum octocyanide, K_3MoCy_8; A. Coehn and O. Schafmeister, the electrokinetic potential of molybdenum; R. J. Piersol, the electronic discharge in vacuum tubes; E. S. Davenport, the surface pitting of tungsten filaments; and H. Nagaoka and T. Fatagami, the spluttering of molybdenum by the disruptive discharge in a magnetic field. W. Ogawa noted that molybdenum-activated galena is a radio detector.

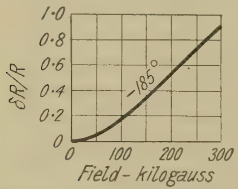


FIG. 7.—The Effect of Magnetic Fields on the Electrical Conductivity.

According to L. Weiss and O. Aichel,[7] molybdenum is para-magnetic. S. Meyer gave for the **magnetic susceptibility,** $0·25 \times 10^{-6}$ mass unit; K. Honda, $0·04 \times 10^{-6}$ to $0·039 \times 10^{-6}$; and M. Owen, $0·60 \times 10^{-6}$ to $0·93 \times 10^{-6}$. The temp., and strength of the magnetic field had only a slight influence on the result. P. Pascal found that the molybdates, unlike the molybdenum salts, are diamagnetic. The subject was studied by D. M. Bose and H. G. Dhar; in its salts, tervalent molybdenum is diamagnetic. P. Kapitza's observations on the effect of strong magnetic fields on the electrical conductivity are summarized in Fig. 7. P. R. Ray studied the magnetic susceptibility of complexes of quinquevalent molybdenum compounds.

References.

[1] J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817 ; *Ann. Chim. Phys.*, (2), **17**. 5, 1921 ; *Pogg. Ann.*, **4**. 153, 1825 ; **6**. 331, 369, 1826 ; **7**. 261, 1826 ; H. Debray, *Compt. Rend.*, **46**. 1095, 1858 ; **56**. 732, 1683 ; **66**. 732, 1868 ; F. Wöhler, *Liebig's Ann.*, **94**. 372, 1855 ; P. J. Hjelm, *Crell's Ann.*, i, 391, 1790 ; i, 179, 248, 266, 353, 429, 1791 ; ii, 59, 1791 ; i, 260, 1792 ; ii, 358, 1792 ; i, 238, 1794 ; C. F. Bucholz, *Scherer's Journ.*, **9**. 485, 1803 ; *Gehlen's Journ.*, **4**. 598. 1803 ; *Phil. Mag.*, **16**. 193, 1803 ; *Nicholson's Journ.*, **20**. 121, 188, 253, 1808 ; *Journ. Mines*, **18**. 241, 1808 ; A. B. du Jassonneix, *Compt. Rend.*, **143**. 169, 1906 ; H. Moissan, *Bull. Soc. Chim.*, (3), **11**. 857, 1894 ; (3), **13**. 966, 1895 ; *Compt. Rend.*, **116**. 1225, 1893 ; **120**. 320, 1895 ; **131**. 998, 1900 ; **142**. 425, 1906 ; J. E. Loughlin, *Amer. Journ. Science*, (2), **45**. 131, 1868 ; K. Wolf, *Das elektrochemische Verhalten des Molybdäns und einiger Molybdänverbindungen*, Aachen, 1917 ; W. Lederer, *Darstellung und Untersuchung reinen, geschmolzen Molybdäns*, Erlangen, 14, 1911 ; L. Weiss and O. Aichell, *Liebig's Ann.*, **337**. 370, 1904 ; C. G. Fink, *Chem. News*, **104**. 34, 1910 ; *Trans. Amer. Electrochem. Soc.*, **17**. 232, 1910 ; **22**. 499, 1912 ; *Chem. Eng.*, **12**. 51, 1910 ; *Met. Chem. Engg.*, **8**. 341. 1910 ; *Chem. News*, **104**. 34, 1911 ; E. C. Bain, *Trans. Amer. Inst. Min. Met. Eng.*, **68**. 625, 1922 ; J. Hengstenberg and H. Mark, *Naturwiss.*, **17**. 433, 1929 ; V. M. Goldschmidt, *Skr. Norske Vid. Akad.*, 2, 1926 ; L. Pauling, *Journ. Amer. Chem. Soc.*, **49**. 765, 1927 ; E. T. Wherry, *Amer. Min.*, **14**. 54, 1929 ; T. Fujiwara, *Mem. Coll. Kyoto Univ.*, **12**. 165, 1929 ; **13**. 109, 1930 ; E. Schmidt, *Zeit. Metallkunde*, **20**. 370, 1928 ; M. Ettisch, M. Polanyi and K. Weissenberg, *Phys. Zeit.*, **22**. 646, 1921 ; *Zeit. phys. Chem.*, **99**. 322, 1921 ; *Zeit. Physik*, **7**. 181, 1921 ; M. Polanyi and K. Weissenberg, *Zeit. tech. Phys.*, **4**. 199, 1923 ; P. W. Bridgman, *Proc. Amer. Acad.*, **58**. 166, 1923 ; L. Vegard, *Phil. Mag.*, (7), **1**. 1151, 1925 ; L. H. Adams, *Journ. Washington Acad.*, **17**. 529, 1927 ; J. Disch, *Zeit. Physik*, **5**. 173, 1921 ; W. Muthmann, L. Weiss and A. Mai, *Liebig's Ann.*, **355**. 100, 1907 ; Z. Jeffries and R. S. Archer, *Chem. Met. Engg.*, **26**. 343, 1922 ; E. Donath and J. Mayrhofer, *Ber.*, **16**. 1588, 1883 ; L. Storch, *ib.*, 16. 2015, 1883 ; N. Stücker, *Sitzber. Akad. Wien*, **114**. 657, 1905 ; J. R. Rydberg, *Zeit. phys. Chem.*, **33**. 353, 1900 ; H. G. Grimm, *ib.*, **122**. 177, 1926 ; F. Simon and W. Zeidler, *ib.*, **123**. 383, 1926 ; W. Zeidler, *Untersuchungen über die spezifische Wärme bei tiefen Temperaturen*, Leipzig, 1926 ; W. R. Mott, *Trans. Amer. Electrochem. Soc.*, **34**. 355, 1918 ; T. W. Richards, *Zeit. Elektrochem.*, **13**. 519, 1907 ; T. W. Richards and E. P. Bartlett, *Journ. Amer. Chem. Soc.*, **37**. 470, 1915 ; T. W. Richards and F. G. Jackson, *Zeit. phys. Chem.*, **70**. 414, 1910 ; A. M. Berkenheim, *ib.*, **141**, 35, 1929 ; L. W. Schad and P. Hidnert, *Journ. Franklin Inst.*, **187**. 112, 1919 ; *Bull. Bur. Standards*, **15**. 31, 1919 ; P. Hidnert and W. B. Cero, *ib.*, **20**. 429, 1924 ; *Scient. Paper U.S. Bur. Standards*, 488, 1924 ; B. Beckman, *Phys. Zeit.*, **18**. 507, 1917 ; I. Traube, *Zeit. anorg. Chem.*, **8**. 12, 1895 ; J. A. M. van Liempt, *ib.*, **114**. 105, 1920 ; J. Dewar, *Proc. Roy. Soc.*, **89**. A, 158, 1913 ; T. Barratt and R. M. Winter, *Proc. Phys. Soc.*, **26**. 347, 1914 ; *Ann. Physik*, (4), **77**. 1, 1925 ; P. Nordmeyer, *Ber. deut. phys. Ges.*, **6**. 202, 1908 ; P. Nordmeyer and A. L. Bernoulli, *ib.*, **5**. 175, 1907 ; O. Ruff and O. Goecke, *ib.*, **43**. 1564, 1910 ; M. von Pirani and A. R. Meyer, *ib.*, **14**. 426, 1912 ; M. Pirani and H. Alterthum, *Zeit. Elektrochem.*, **29**. 5, 1923 ; M. Pirani, *Ber. deut. phys. Ges.*, **14**. 426, 1912 ; E. Defacqz and M. Guichard, *Ann. Chim. Phys.*, (7), **24**. 139, 1901 ; H. V. Regnault, *ib.*, (2), **73**. 5, 1840 ; A. de la Rive and F. Marcet, *ib.*, (2), **75**. 113, 1840 ; M. Grube, *Zeit. Ges. Giessereipr.*, **47**. 173, 1926 ; *Chim. Ind.*, **18**. 68, 1927 ; H. von Wartenberg, *Verh. deut. phys. Ges.*, **12**. 121, 1910 ; W. P. Sykes, *Trans. Amer. Inst. Met. Eng.*, **64**. 780, 1921 ; E. W. Engle, *ib.*, **71**. 691, 1925 ; C. W. Waidner and G. K. Burgess, *The Measurement of High Temperatures*, New York, 446, 493, 1912 ; G. K. Burgess, *Journ. Washington Acad.*, **1**. 16, 1912 ; M. Delépine, *Bull. Soc. Chim.*, (3), **29**. 1166, 1903 ; W. G. Mixter, *Amer. Journ. Science*, (4), **29**. 488, 1910 ; A. W. Hull, *Phys. Rev.*, (2), **17**. 571, 1921 ; A. W. Hull and W. P. Davey, *ib.*, (2), **17**. 549, 1921 ; W. P. Davey, *Journ. Amer. Opt. Soc.*, **5**. 479, 1921 ; *Gen. Elect. Rev.*, **25**. 565, 1922 ; *Phys. Rev.*, (2), **23**. 292, 1924 ; (2), **25**. 753, 1925 ; M. L. Huggins, *ib.*, (2), **28**. 1086, 1926 ; A. L. Kimball and D. E. Lovell, *ib.*, (2), **30**. 948, 1927 ; E. Podszus, *German Pat.*, *D.R.P.* 290606, 1913 ; 293963, 1914 ; E. Siedschlag, *Zeit. anorg. Chem.*, **131**. 191, 1923 ; W. Herz, *ib.*, **94**. 8, 1916 ; **117**. 116, 1928 ; **180**. 284, 1929 ; J. Maydel, *ib.*, **178**. 113, 1929 ; **186**. 289, 1930 ; F. Wüst, A. Meuthen and R. Durrer, *Ver. deut. Ing. Forsch.*, 204, 1918 ; W. Widder, *Phys. Zeit.*, **26**. 618, 1925 ; E. D. Eastman, A. M. Williams and T. F. Young, *Journ. Amer. Chem. Soc.*, **46**. 1184, 1924 ; G. N. Lewis, G. E. Gibson and W. M. Latimer, *ib.*, **44**. 1008, 1922 ; W. M. Latimer, *ib.*, **44**. 2136, 1922 ; E. D. Eastman, *ib.*, **45**. 80, 1923 ; W. H. Rodebush, *ib.*, **45**. 997, 1923 ; J. E. Moose and S. W. Parr, *ib.*, **46**. 2656, 1924 ; R. C. Tolman, *ib.*, **42**. 1185, 1920 ; B. Bruzs, *Journ. Phys. Chem.*, **31**. 681, 1927 ; H. A. Jones, I. Langmuir and G. M. J. Mackay, *Phys. Rev.*, (2), **30**. 201, 1927 ; I. Langmuir, *Trans. Amer. Electrochem. Soc.*, **29**. 125, 1916 ; *Phys. Rev.*, (2), **4**. 384, 1914 ; K. Weissenberg, *Zeit. Kryst.*, **61**. 58, 1924 ; A. G. Worthing, *Journ. Franklin Inst.*, **149**. 499, 1925 ; *Phys. Rev.*, (2), **25**. 846, 1925 ; (2), **21**. 705, 1923 ; (2), **28**. 190, 1926 ; R. C. Smith, *Journ. Chem. Soc.*, **123**. 2088, 1923 ; S. T. Konobejevsky, *Zeit. Physik*, **39**. 415, 1926 ; J. Königsberger, *ib.*, **41**. 729, 1926 ; Z. Jeffries and R. S. Archer, *Chem. Met. Engg.*, **27**. 747, 1922 ; P. Stoll, *Arch. Sciences Genève*, (5), **3**. 546, 1922 ; A. E. van Arkel, *Physica*, **6**. 64, 1926 ; C. Zwikker, *Physica*, **7**. 71, 1927 ; E. Edwards, I. Bowen and S. Alty, *Phil. Mag.*, (7), **2**. 321, 1926 ; C. C. van Voorhis, *Phys. Rev.*, (2), **30**. 318, 1927 ; H. A. Jones, *ib.*, (2), **30**. 332, 1927 ; T. E. Stern, *ib.*, (2), **32**. 298, 1928 ; D. Cooper and G. O. Langstroth, *ib.*, (2), **33**. 243, 1929 ; P. Nordmeyer and A. L. Bernoulli, *Verh. deut. phys. Ges.*, **9**. 175, 1907 ; R. D. Kleeman, *Journ. Phys. Chem.*, **31**. 1669, 1927 ; J. Laissus, *Rev. Mét.*, **24**. 345, 1927 ; J. C. Slater, *Phys. Rev.*, (2), **36**. 57, 1930 ; W. Hume-Rothery, *Phil. Mag.*, (7), **10**. 217, 1930 ; T. Fujiwara, *Mem. Coll. Kyoto*,

13. 109, 1930 ; P. W. Bridgman, *Proc. Amer. Acad.*, **64.** 39, 1929 ; F. J. Wilkins, *Nature,* **125.** 236, 1930 ; G. Grube and F. Lieberwirth, *Zeit. anorg. Chem.*, **188.** 274, 1930 ; J. A. M. van Liempt, *ib.*, **189.** 287, 1930 ; P. Ludwik, *Zeit. Ver. deut. Ing.*, **59.** 657, 1915 ; P. Vinassa, *Gazz. Chim. Ital.*, **58.** 178, 1928.

[2] W. W. Coblentz, *Journ. Franklin Inst.*, **170.** 169, 1910 ; A. G. Worthing, *ib.*, **199.** 549, 1925 ; *Journ. Amer. Opt. Soc.*, **13.** 635, 1926 ; *Phys. Rev.*, (2), **21.** 705, 1923 ; (2), **25.** 846, 1925 ; (2), **28.** 190, 1926 ; *Journ. Amer. Opt. Soc.*, **13.** 635, 1926 ; G. Jaffé, *Ann. Physik*, (4), **45.** 1217, 1915 ; C. Davisson and L. H. Germer, *Phys. Rev.*, (2), **20.** 300, 1922 ; R. L. Petry, *ib.*, (2), **26.** 346, 1925 ; M. J. Martin, *ib.*, (2), **33.** 991, 1929 ; S. Dushman and J. W. Ewald, *Gen. Elect. Rev.*, **26.** 154, 1923 ; *Phys. Rev.*, (2), **20.** 109, 1922 ; S. Dushman, H. N. Rowe and C. A. Kidner, *ib.*, (2), **21.** 207, 1923 ; (2), **25.** 338, 1925 ; A. W. Hull and J. M. Hyatt, *ib.*, (2), **29.** 214, 1927 ; J. M. Hyatt and H. A. Smith, *ib.*, (2), **32.** 929, 1928 ; C. C. van Voorhis and K. T. Compton, *ib.*, (2), **29.** 909, 1927 ; (2), **36.** 1435, 1930 ; W. R. Ham. *ib.*, (2), **29.** 908, 1927 ; C. C. van Voorhis, *ib.*, (2), **30.** 318, 1927 ; R. J. Piersol, *ib.*, (2), **25.** 112, 1925 ; W. R. Ham and M. W. White, *ib.*, (2), **23.** 777, 1924 ; (2), **27.** 111, 510, 1926 ; R. C. Gibbs and H. E. White, *ib.*, (2), **31.** 520, 1928 ; H. R. Kiehl, W. R. Ham, M. W. White and W. P. Davey, *ib.*, (2), **33.** 1089, 1929 ; W. J. Jackson, *ib.*, (2), **28.** 524, 1926 ; (2), **30.** 473, 1927 ; A. T. Waterman, *ib.*, (2), **24.** 366, 1924 ; A. L. Helfgott, *Zeit. Physik*, **49.** 555, 1928 ; E. S. Lamar and W. E. Deming, *Phil. Mag.*, (7), **9.** 28, 1929 ; C. Zwikker, *Proc. Acad. Amsterdam*, **29.** 792, 1926 ; **30.** 853, 1927 ; *Versl. Akad. Amsterdam*, **35.** 336, 1926 ; **36.** 856, 1927 ; *Physica*, **7.** 71, 1927 ; S. C. Roy, *Proc. Roy. Soc.*, **112.** A, 599, 1926 ; H. Klumb, *Ueber den Einfluss der Gasbeladung auf die lichtelektrische Empfindlichkeit der Metalle*, Berlin, 1928 ; *Zeit. Physik*, **47.** 652, 1928 ; R. H. Fowler, *Proc. Roy. Soc.*, **117.** A, 549, 1928 ; M. Pirani and H. Schönborn, *Naturwiss.*, **15.** 767, 1927 ; H. B. Wahlin, *Nature*, **123.** 912, 1929 ; E. Meyer, *Ann. Physik*, (5), **4.** 357, 1930 ; *Ueber die Elektronen- und positive Ionemission von Wolfram-, Molybdan-, und Tantalglühfäden in Kaliumdampf*, Berlin, 1930 ; E. Rupp, *Ann. Physik*, (5), **5.** 453, 1930 ; M. L. E. Oliphant, *Proc. Roy. Soc.*, **127.** A, 373, 1930 ; L. P. Smith, *Phys. Rev.*, (2), **35.** 381, 1930 ; T. Soller, *ib.*, (2), **36.** 1212, 1930 ; L. J. Haworth, *ib.*, (2), **37.** 93, 1931 ; E. Patai, *Zeit. Physik*, **59.** 697, 1930.

[3] R. Bunsen, *Liebig's Ann.*, **138.** 257, 1866 ; R. T. Simmler, *Beiträge zur chemischen Analyse durch Spectralbeobachtungen*, Bern, 1861 ; *Pogg. Ann.*, **115.** 242, 425, 1862 ; C. C. Kiess and W. F. Meggers, *Bull. Bur. Standards*, **16.** 51, 1920 ; C. Horner, *Chem. News*, **29.** 66, 1874 ; W. A. Miller, *Phil. Trans.*, **152.** 861, 1862 ; R. J. Lang, *ib.*, **224.** A, 371, 1924 ; J. N. Lockyer, *ib.*, **172.** 561, 1881 ; *Proc. Roy. Soc.*, **27.** 279, 1878 ; *Tables of Wave-lengths of enhanced Lines*, London, 1906 ; H. Kayser, *Handbuch der Spectroscopie*, Leipzig, **5.** 772, 1910 ; R. Thalén, *Om spectralanalyse*, Upsala, 1866 ; *Nova Acta Soc. Upsala*, (3), **6.** 9, 1868 ; E. Demarçay, *Spectres électriques*, Paris, 1895 ; F. Exner and E. Haschek, *Wellenlangentabellen für spectralanalytische Untersuchungen auf der ultravioletten Bogenspectren der Elemente*, Leipzig, 1904 ; *Wellenlangentabellen für spectralanalytische Untersuchungen auf der ultravioletten Funkenspectren der Elemente*, Leipzig, 1902 ; *Die Spectren der Elemente bei normalen Druck*, Leipzig, 1912 ; *Sitzber. Akad. Wien*, **104.** 909, 1895 ; **105.** 503, 1896 ; **106.** 36, 1897 ; J. M. Eder and E. Valenta, *ib.*, **118.** 511, 1909 ; J. Formanek, *Zeit. anal. Chem.*, **39.** 680, 1900 ; *Die qualitative Spectralanalyse anorganischer und organischer Körper*, Berlin, 154, 1905 ; A. Hagenbach and H. Konen, *Atlas der Emissionspectra*, Jena, 1905 ; H. Geisler, *Zur anomalen Dispersion des Lichtes in Metalldämpfen*, Bonn, 1909 ; *Zeit. wiss. Photochem.*, **7.** 80, 1909 ; C. Weigand, *ib.*, **11.** 261, 1912 ; M. Puhlmann, *Messungen im Molybdänspektrum nach internationalen Normalen*, Leipzig, 1917 ; *Zeit. wiss. Photochem.*, **17.** 97, 1918 ; J. E. Paulson, *ib.*, **18.** 202, 1918 ; R. Jack, *Zeeman effect an Wolfram und Molybdän*, Göttingen, 1908 ; *Proc. Roy. Soc. Edin.*, **29.** 75, 1908 ; *Ann. Physik*, (4), **28.** 1032, 1909 ; A. G. G. Leonard, *Proc. Roy. Soc. Dublin*, (2), **11.** 270, 1908 ; W. N. Hartley and H. Ramage, *Trans. Roy. Soc. Dublin*, (2), **7.** 339, 1901 ; P. G. Nutting, *Astrophys. Journ.*, **23.** 64, 1906 ; W. J. Humphreys, *ib.*, **6.** 169, 1897 ; O. Lohse, *Publ. Astrophys. Obs. Potsdam*, **12.** 109, 1902 ; B. Hasselberg, *Svenska Akad. Handl.*, **36.** 2, 1902 ; *Astrophys. Journ.*, **16.** 300, 1902 ; **17.** 20, 1903 ; M. A. Catalan, *Compt. Rend.*, **176.** 247, 1063, 1923 ; *Anal. Fis. Quim.*, **21.** 213, 527, 1923 ; M. Eppley, *Journ. Franklin Inst.*, **201.** 333, 1926 ; G. Merz, *Journ. prakt. Chem.*, (1), **80.** 495, 1860 ; *Chem. News*, **3.** 146, 1861 ; C. F. Plattner, *Die Probirkunst mit dem Löthrohre*, Leipzig, 1835 ; F. Croze, *Compt. Rend.*, **177.** 1285, 1923 ; E. O. Hulburt, *Phys. Rev.*, (2), **24.** 129, 1924 ; (2), **25.** 888, 1925 ; J. C. McLennan and A. C. Lewis, *Proc. Roy. Soc.*, **98.** A, 109, 1920 ; E. Wilhelmy, *Ann. Physik*, (4), **80.** 305, 1926 ; *Naturwiss.*, **13.** 49, 1926 ; H. B. Dorgels, *Zeit. Physik*, **36.** 467, 1926 ; C. C. Kiess, *Bull. Bur. Standards*, **19.** 113, 1923 ; C. C. Kiess and O. Laporte, *Science*, (2), **63.** 234, 1926 ; W. F. Meggers and C. C. Kiess, *Journ. Amer. Opt. Soc.*, **12.** 417, 1926 ; *Bull. Bur. Standards*, **16.** 51, 1920 ; O. Laporte, *ib.*, **13.** 1, 1926 ; M. Kimura and G. Nakamura, *Science Papers Japan Inst. Phys. Chem. Research*, **3.** 51, 1925 ; H. Nagaoka, D. Nukiyarna, and T. Futagami, *Proc. Acad. Japan*, **3.** 392, 398, 403, 409, 415, 1927 ; E. Paulson, *Beiträge zur Kenntnis der Linenspektrum*, Lund, 1914 ; E. J. Allin and H. J. C. Ireton, *Trans. Roy. Soc. Canada*, (3), **21.** 127, 1927 ; T. Aden, *Die Aenderungen der Absorptionsspektren im sichtbaren und ultravioletten Gebiet bei Aggregation in Lösungen schwacher anorganischer Säuren und ihrer Salze*, Göttingen, 1929 ; R. C. Gibbs and H. E. White, *Phys. Rev.*, (2), **31.** 520, 1928 ; S. Kato, *Science Papers Inst. Phys. Chem. Research*, **13.** 7, 1930 ; W. H. Fulweiler and J. Barnes, *Journ. Franklin Inst.*, **194.** 83, 1922,

[4] H. R. Robinson and A. M. Cassie, *Proc. Roy. Soc.*, **113.** A, 282, 1926 ; H. R. Robinson and C. L. Young, *ib.*, **128.** A, 92, 1930 ; H. R. Robinson, *ib.*, **104.** A, 455, 1923 ; L. H. Martin, *ib.*, **115.** A, 420, 1927 ; S. Tanaka and J. Tsutsumi, *Mem. Coll. Kyoto*, **7.** 1, 1923 ; S. K. Allison,

Nature, **115**. 978, 1925 ; S. K. Allison and W. Duane, *Proc. Nat. Acad.*, **10**. 381, 1924 ; **11**. 25, 1925 ; S. K. Allison, G. L. Clark and W. Duane, *ib.*, **10**. 379, 1924 ; W. Duane and R. A. Paterson, *Phys. Rev.*, (2), **19**. 542, 1922 ; *Proc. Nat. Acad.*, **8**. 85, 1922 ; E. O. Wollan, *ib.*, **14**. 864, 1928 ; S. K. Allison and A. H. Armstrong, *Phys. Rev.*, (2), **25**. 882, 1925 ; (2), **26**. 701, 1925 ; *Proc. Nat. Acad.*, **11**. 563, 1925 ; S. K. Allison and J. H. Williams, *Phys. Rev.*, (2), **35**. 135, 149, 1476, 1496, 1930 ; G. L. Clark, W. W. Stifler and W. Duane, *ib.*, (2), **23**. 551, 1924 ; *Proc. Nat. Acad.*, **10**. 41, 92, 148, 1924 ; **11**. 173, 563, 1925 ; **9**. 413, 419, 1923 ; F. C. Blake and W. Duane, *Phys. Rev.*, (2), **10**. 98, 697, 1917 ; J. W. M. du Mond, *ib.*, (2), **36**. 146, 1930 ; F. L. Nutting, *ib.*, (2), **36**. 1267, 1930 ; J. M. Cork, *ib.*, (2), **35**. 1456, 1930 ; (2), **36**. 665, 1930 ; N. S. Gingrich, *ib.*, (2), **35**. 1444, 1930 ; F. W. Warburton and F. K. Richtmyer, *ib.*, (2), **23**. 291, 1924 ; G. E. M. Jauncey, *ib.*, (2), **25**. 723, 1925 ; L. Rolla and G. Piccardi, *Atti Accad. Lincei*, (6), **2**. 173, 1925 ; F. K. and R. D. Richtmyer, *Phys. Rev.*, (2), **34**. 574, 1929 ; F. K. Richtmyer and R. C. Spencer, *ib.*, (2), **23**. 550, 1924 ; F. K. Richtmyer and L. S. Taylor, *ib.*, (2), **29**. 606, 1927 ; A. P. R. Wadland, *ib.*, (2), **32**. 841, 1928 ; M. A. Rewutzka, *Zeit. Physik*, **57**. 556, 1929 ; F. K. Richtmyer, *Phil. Mag.*, (7), **6**. 64, 1928 ; *Phys. Rev.*, (2), **17**. 264, 1921 ; (2), **18**. 13, 1921 ; (2), **26**. 724, 1925 ; (2), **27**. 1, 1926 ; (2), **30**. 755, 1927 ; P. A. Ross, *ib.*, (2), **26**. 281, 282, 1925 ; M. Balderston, *ib.*, (2), **27**. 696, 1926 ; Y. H. Woo, *ib.*, (2), **28**. 427, 1927 ; A. H. Compton and Y. H. Woo, *ib.*, (2), **23**. 763, 1924 ; G. E. M. Jauncey and A. H. Compton, *Nature*, **120**. 549, 1927 ; A. H. Compton, *Phil. Mag.*, (7), **8**. 961, 1929 ; *Phys. Rev.*, (2), **35**. 127, 1930 ; A. H. Compton and R. L. Doan, *Proc. Nat. Acad.*, **11**. 598, 1925 ; J. H. Purks and C. M. Slack, *Phys. Rev.*, (2), **29**. 352, 1927 ; B. Davis and H. Purks, *ib.*, **13**. 419, 1927 ; **14**. 172, 1928 ; *Phys. Rev.*, (2), **31**. 306, 1119, 1928 ; (2), **32**. 336, 1928 ; H. Purks, *ib.*, (2), **31**. 931, 1928 ; (2), **33**. 1089, 1929 ; H. A. Erickson, *ib.*, (2), **32**. 791, 1928 ; A. Bouwers, *Physica*, **5**. 8, 1925 ; F. Wagner, *Phys. Zeit.*, **18**. 405, 432, 461, 488, 1917 ; A. Dauvillier, *Compt. Rend.*, **174**. 443, 1922 ; **178**. 1522, 1924 ; **183**. 193, 1926 ; P. Anger, *ib.*, **187**. 1141, 1928 ; D. Coster and F. P. Mulder. *Zeit. Physik*, **38**. 264, 1926 ; W. Ehrenberg and H. Mark, *ib.*, **42**. 807, 1927 ; W. Ehrenberg and G. von Susich, *ib.*, **42**. 823, 1927 ; D. Coster, I. Nitta, and W. J. Thijssen, *Nature*, **123**. 642, 1929 ; D. Coster, *Phil. Mag.*, (6), **43**. 1070, 1922 ; *Compt. Rend.*, **174**. 378, 1922 ; M. de Broglie, *ib.*, **163**. 87, 1916 ; **172**. 274, 527, 1921 ; J. Thibaud, *ib.*, **185**. 62, 1927 ; M. A. Catalan, *ib.*, **176**. 1063, 1923 ; M. Siegbahn and E. Friman, *Ann. Physik*, (4), **49**. 611, 1916 ; M. Siegbahn and A. Larsson, *Ark. Mat. Fys.*, **18**. 18, 1924 ; M. Siegbahn, *Jahrb. Rad. Elektron.*, **13**. 296, 1916 ; **18**. 240, 1918 ; *Journ. Phys. Rad.*, (6), **6**. 228, 1925 ; *Zeit. Physik.*, **50**. 443, 1928 ; E. Hjalmar, *ib.*, **3**. 262, 1920 ; A. Leide, *ib.*, **39**. 686, 1926 ; A. Jönsson, *ib.*, **41**. 221, 1927 ; **43**. 845, 1927 ; **46**. 383, 1928 ; K. A. Wingärdh, *ib.*, **8**. 363, 1922 ; B. Walter, *ib.*, **30**. 357, 1924 ; H. G. J. Moseley, *Phil. Mag.*, (6), **27**. 703, 1914 ; R. Whiddington, *ib.*, (6), **43**. 1116, 1922 ; R. A. Houstoun, *ib.*, (7), **2**. 512, 1926 ; B. B. Ray, *ib.*, (6), **48**. 707, 1926 ; L. M. Alexander, *ib.*, (7), **4**. 670, 1927 ; L. R. G. Treloar, *ib.*, (7), **6**. 1008, 1928 ; J. Malmer, *ib.*, (6), **28**. 787, 1915 ; T. E. Auren, *ib.*, (6), **33**. 471, 1917 ; D. Nasledoff and P. Sharawsky. *Phys. Zeit.*, **28**. 549, 1927 ; *Zeit. Physik*, **42**. 870, 1927 ; **43**. 431, 1927 ; W. Bothe and H. Franz, *ib.*, **52**. 466, 1928 ; G. Kettmann, *ib.*, **53**. 198, 1929 ; S. Björek, *ib.*, **53**. 228, 1929 ; M. J. Druyvesteyn, *ib.*, **43**. 707, 1927 ; A. P. R. Wadlund, *Proc. Nat. Acad.*, **14**. 588, 1928 ; H. Hirata, *Proc. Roy. Soc.*, **105**. A, 40, 1924 ; P. Günther, *Naturwiss.*, **14**. 1118, 1926 ; J. Schrör, *Ann. Physik*, (4), **80**. 297, 1926 ; G. Hagen, *ib.*, (4), **78**. 407, 1925 ; F. Kirchner, *ib.*, (4), **78**. 421, 1925 ; J. E. P. Wagstaff, *Phil. Mag.*, (6), **47**. 84, 1924 ; A. Larsson, *ib.*, (7), **3**. 1136, 1927 ; D. L. Webster, *Proc. Nat. Acad.*, **10**. 186, 1924 ; *Phys. Rev.*, (2), **19**. 543, 1922 ; D. L. Webster and A. E. Hennings, *ib.*, (2), **21**. 301, 312, 1923 ; C. B. Bozzani and C. T. Chu, *Journ. Franklin Inst.*, **197**. 183, 1924 ; O. W. Richardson and C. B. Bozzani, *Phil. Mag.*, (6), **42**. 1015, 1921 ; O. W. Richardson and F. S. Robertson, *Proc. Roy. Soc.*, **115**. A, 280, 1927 ; **124**. A, 188, 1929 ; G. B. Bandopadhyaya, *ib.*, **120**. A, 46, 1928 ; L. P. Davis, *ib.*, **124**. A, 268, 1929 ; W. Herz, *Zeit. anorg. Chem.*, **117**. 116, 1928 ; W. Bothe, *Phys. Zeit.*, **29**. 891, 1928 ; M. Ishino and S. Kawata, *Mem. Coll. Kyoto*, **10**. 311, 1927 ; J. Zahradnicek, *Zeit. Physik*, **60**. 712, 1930 ; D. Mitchell and B. Davis, *Phys. Rev.*, (2), **31**. 3111, 1928 ; (2), **33**. 292, 1929 ; E. N. Coade, *ib.*, (2), **36**. 1109, 1930 ; R. W. G. Wyckoff, *ib.*, (2), **36**. 1116, 1930 ; C. C. von Voorhrs and K. T. Compton, *ib.*, (2), **36**. 1435, 1930 ; J. Hengstenberg, *Metallwirtschaft*, **9**. 465, 1930 ; B. Davis and H. Purks, *Proc. Nat. Acad.*, **13**. 419, 1927 ; **14**. 172, 1928 ; J. Valasek, *Phys. Rev.*, (2), **35**. 291, 1930 ; (2), **36**. 1523, 1930 ; H. Monk and G. von Susich, *Zeit. Physik*, **65**. 253, 1930 ; F. Wisshak, *Ann. Physik*, (5), **5**. 507, 1930.

[5] N. Piltschikoff, *Phys. Zeit.*, **7**. 69, 1906 ; M. J. Martin, *Phys. Rev.*, (2), **33**. 991, 1929 ; J. Lifschitz, *Proc. Acad. Amsterdam*, **26**. 561, 1923 ; R. T. Dufford, *Journ. Amer. Opt. Soc.*, **18**. 17, 1929 ; T. Pavolini, *Ind. Chimica*, **5**. 1107, 1930.

[6] E. Dubois, *Compt. Rend.*, **186**. 1832, 1928 ; P. Kapitza, *Proc. Roy. Soc.*, **105**. A, 691, 1924 ; **106**. A, 602, 1924 ; **115**. A, 658, 1927 ; **119**. A, 358, 1928 ; **123**. A, 292, 342, 1929 ; C. G. Fink, *Chem. News*, **104**. 34, 1910 ; *Trans. Amer. Electrochem. Soc.*, **17**. 232, 1910 ; **22**. 499, 1912 ; *Chem. Eng.*, **12**. 51, 1910 ; *Met. Chem. Engg.*, **8**. 341, 1910 ; *Chem. News*, **104**. 34, 1911 ; G. C. Schmidt, *Zeit. phys. Chem.*, **106**. 105, 1923 ; L. Holborn, *Zeit. Elektrochem.*, **25**. 234, 1919 ; *Zeit. Physik*, **8**. 58, 1922 ; *Ann. Physik*, (4), **59**. 145, 1919 ; C. E. Blom, *ib.*, (4), **42**. 1402, 1903 ; *Phys. Rev.*, (2), **13**. 308, 1919 ; A. A. Somerville, *ib.*, (1), **30**. 268, 532, 1910 ; (1), **31**. 261, 1911 ; K. F. Herzfeld, *ib.*, (2), **29**. 701, 1927 ; A. G. Worthing, *ib.*, (2), **28**. 120, 1926 ; B. Beckman, *Phys. Zeit.*, **18**. 507, 1917 ; S. J. French and L. Kahlenberg, *Trans. Amer. Electrochem. Soc.*, **54**. 163, 1928 ; A. C. Krüger and L. Kahlenberg, *ib.*, **58**. 107, 1930 ; A. Coehn and O. Schafmeister, *Zeit. phys. Chem.*, **125**. 401, 1927 ; O. Collenberg, *ib.*, **109**. 353, 1924 ; O. Collenberg and B. Andersen, *Zeit. Elektrochem.*, **31**.

558, 1920 ; W. Muthmann and F. Fraunberger, *Sitzber. Akad. München*, (2), **34**. 201, 212, 1904 ; A. S. Russell and S. W. Rowell, *Journ. Chem. Soc.*, 1881, 1926 ; S. Morugina, *Zeit. tech. Phys.*, **7**. 486, 1926 ; L. Marino, *Gazz. Chim. Ital.*, **35**. ii, 193, 1905 ; H. Kuessner, *Ueber das anodische Verhalten des Molybdäns, Mangans, Chroms und Tantals*, Halle a. S., 1910 ; *Zeit. Elektrochem.*, **16**. 754, 1910 ; L. Lorenz, *Elektrochemisches Praktikum*, Göttingen, 181, 1901 ; K. Wolf, *Das elektrochemische Verhalten des Molybdäns und einiger Molybdänsverbindungen*, Aachen, 1917 ; P. W. Bridgman, *Proc. Amer. Acad.*, **52**. 573, 1917 ; **53**. 269, 1918 ; W. Geiss and J. A. M. van Liempt, *Zeit. Metallkunde*, **17**. 194 ; 1925 ; *Zeit. Physik*, **41**. 867, 1927 ; Z. A. Epstein, *ib.*, **32**. 620, 1925 ; A. Thiel and W. Hammerschmidt, *Zeit. anorg. Chem.*, **132**. 15, 1923 ; R. D. Kleeman and W. Frederickson, *Phys. Rev.*, (2), **19**. 409, 1923 ; R. J. Piersol, *ib.*, (2), **25**. 112, 1925 ; H. Nagaoka and T. Fatagami, *Proc. Acad. Tokyo*, **3**. 643, 1927 ; A. Schulze, *Zeit. Metallkunde*, **15**. 159, 1923 ; **16**. 50, 1924 ; E. S. Davenport, *Trans. Amer. Inst. Min. Eng.—Metals Div.*, 413, 434, 1927 ; C. Zwikker, *Physica*, **7**. 71, 1927 ; H. K. Onnes and W. Tuyn, *Comm. Phys. Lab. Leiden*, Suppl. 58, 1926 ; A. T. Waterman, *Phil. Mag.*, (7), **6**. 965, 1928 ; W. Ogawa, *Journ. Japan. Soc. Chem. Ind.*, **31**. 486, 1928 ; E. Blumenthal, *Ann. Physik*, (5), **7**. 470, 1930 ; U. Fischer, *Zeit. phys. Chem.*, **8**. B, 207, 1930 ; H. Rolnick, *Phys. Rev.*, (2), **36**. 506, 1930 ; M. Forro and E. Patai, *Zeit. Physik*, **63**. 444, 1930 ; L. O. Bannister and U. R. Evans, *Journ. Chem. Soc.*, 3163, 1930 ; J. C. McLennan, L. E. Howlett and J. O. Wilhelm, *Trans. Roy. Soc. Canada*, (3), **23**. 287, 1930 ; W. Rohn, *Zeit. Metallkunde*, **16**. 297, 1924 ; O. Bauer, *Internat. Zeit. Metallog.*, **10**. 129, 1919.

[7] L. Weiss and O. Aichel, *Liebig's Ann.*, **337**. 370, 1904 ; S. Meyer, *Wied. Ann.*, **68**. 324, 1899 ; *Monatsh.*, **20**. 369, 1899 ; D. M. Bose and H. G. Dhar, *Zeit. Physik*, **31**. 716, 1928 ; K. Honda, *Ann. Physik*, (4), **32**. 1027, 1910 ; M. Owen, *ib.*, (4), **37**. 657, 1912 ; P. Pascal, *Compt. Rend.*, **147**. 742, 1908 ; P. Kapitza, *Proc. Roy. Soc.*, **123**. A. 292, 342, 1929 ; P. R. Ray, *Journ. Indian Chem. Soc.*, **7**. 741, 1930.

§ 5. The Chemical Properties of Molybdenum

F. Fischer and F. Schrötter[1] observed no reaction when molybdenum was sparked beneath liquid **argon.** No *molybdenum hydride* has been prepared. According to A. Vandenberghe, J. H. Müller, and W. Lederer, molybdenum does not in general absorb **hydrogen,** but if the metal is in a fine state of subdivision, L. Hamburger found that it can occlude some hydrogen which is again given off at 300°. E. Martin made observations on this subject. J. A. Kendall made a hot molybdenum film through which hydrogen was passing serve as one element of a galvanic cell. According to J. J. Berzelius, molybdenum loses its metallic lustre by exposure to **air** for some days at ordinary temp. J. Férée found that pyrophoric molybdenum which has been heated to 400° is no longer spontaneously inflammable in air. Under ordinary conditions, molybdenum is stable in air at ordinary temp. W. Lederer, however, said that the surface of the metal exposed to air gradually acquires a brass-yellow film. According to C. Matignon and G. Desplantes, finely-divided molybdenum oxidizes at ordinary temp. in air in the presence of aq. ammonia. J. J. Berzelius said that when heated in air it becomes first brown, then blue, and lastly, nearly white ; and, if the temp. is high enough, it emits light, gives off fumes, and forms crystalline molybdenum trioxide. H. Moissan added that if the metal be free from carbon and silicon, it oxidizes but little in air below a red-heat ; but at a dull red-heat, it oxidizes superficially in air, and at 600° oxidation becomes marked, and molybdenum trioxide slowly volatilizes. The trioxide is the product of the oxidation in air at high temp., but in the oxyhydrogen flame, it is accompanied by the blue oxide. N. B. Pilling and R. E. Bedworth studied the oxidation in air of this family of metals. The metal in **oxygen** at 500° to 600° burns to the trioxide. W. Lederer added that when the metal is warmed in oxygen, it acquires a film coloured successively yellow, brown, blue, bluish-red, and black, its surface then glows, and the black substance suddenly bursts into a pale white flame forming the trioxide. L. O. Bannister discussed the coloured oxide films on molybdenum. C. F. Bucholz, and J. J. Berzelius found that **water** does not oxidize the metal at ordinary temp., and H. Moissan added that if the metal be free from carbon and silicon, it can be kept unchanged in water for several days, even when the water is charged with carbon dioxide. W. Lederer found that after molybdenum has stood in contact with water for a week, it acquires a blue film of a lower oxide, and this then becomes yellowish-brown. With water-vapour, free from air, red-hot molybdenum becomes yellow, then brown, and blue, whilst W. Guertler and

T. Liepus observed no action with sat. chlorine-water during 8 days ; H. V. Regnault observed that molybdenum decomposes water-vapour at a red-heat, first forming a blue oxide, and then molybdenum trioxide. M. Guichard said that steam first oxidizes molybdenum at 700°. W. Guertler and T. Liepus observed that sea-water, aerated sea-water, and aerated rain-water have no action on molybdenum during 8 days' exposure. By slowly oxidizing this metal in water-vapour alone, or admixed with hydrogen, no oxides other than the di- and trioxides are formed. G. Chaudron studied the equilibrium conditions in the balanced reaction : $Mo+2H_2O \rightleftharpoons MoO_2+2H_2$ over the temp. range 700° to 1100°. W. Guertler and T. Liepus observed no action during 24 hrs.' exposure to a soln. of **hydrogen dioxide** in soda-lye ; but L. J. Thénard found that the metal is oxidized. C. G. Fink, and W. G. Mixter found the molybdenum is readily attacked by melting **sodium dioxide ;** J. A. Hedvall and N. von Zweigbergk studied the action of **barium dioxide ;** and H. Moissan that there is an intense development of heat and light when a mixture of molybdenum and **lead dioxide** is heated.

According to H. Moissan, **fluorine** has no action on molybdenum *en masse* at ordinary temp., but it acts on the coarsely-powdered metal with incandescence, and the formation of a volatile fluoride. J. J. Berzelius found that **chlorine** does not act on the metal at ordinary temp.—W. Lederer said that a bluish-black film is formed—but at a gentle heat, the surface exhibits a transient glow, and a dark red vapour is formed. H. Moissan observed that chlorine attacks the metal at a dull-red heat without incandescence ; and **bromine** combines with the metal, though not energetically at a bright red-heat. C. W. Blomstrand observed that with chlorine or bromine, several chlorides or bromides are formed, and if the halogen is mixed with air, oxyhalides are produced. J. J. Berzelius found that chlorine-water oxidizes molybdenum, and W. Lederer, that bromine-water is decolorized by shaking it with powdered molybdenum. J. J. Berzelius, and H. Moissan found that **iodine** has no action on red-hot molybdenum. O. Ruff and H. Krug found **chlorine trifluoride** attacks the metal with incandescence. J. J. Berzelius, and C. F. Bucholz observed that **hydrofluoric acid** has no action on molybdenum, and H. Moissan added that hydrofluoric acid is without action except in the presence of nitric acid when the metal is rapidly attacked. W. E. Ruder said that the metal is not attacked by this acid hot or cold. J. J. Berzelius, and C. F. Bucholz said that the metal is not attacked by **hydrochloric acid ;** W. E. Ruder said that the dil. acid slowly attacks molybdenum at 110° forming some black oxide, probably Mo_2O_3. The loss in weight was 20·3 per cent. after 18 hours. The more concentrated acid (1·15) has a much slower action. After keeping the metal for 18 hours in this acid at 110°, the total loss of metal was only 0·34 per cent. and the surface was still bright. W. Guertler and T. Liepus observed no action during 48 hrs.' exposure to 10 and 36 per cent. hydrochloric acid ; W. Rohn, that the cold 10 per cent. hydrochloric acid dissolved only 0·01 per cent. in 24 hrs. in the cold, and with the hot acid 0·0015 was dissolved in one hour, and 0·08 per cent. in 24 hrs. ; W. Lederer, that boiling dil. hydrochloric acid has no action, but the hot conc. acid very slowly attacks the metal. H. Moissan found that fused **potassium chlorate** attacks the metal violently.

H. Moissan found that **sulphur** has no action on molybdenum at 440° ; but **hydrogen sulphide** at 1200° converts the metal into a sulphide closely resembling molybdenite. J. Férée found that pyrophoric molybdenum at ordinary temp. or when gently heated does not react with hydrogen sulphide. E. W. Engle found that molybdenum is resistant to corrosion by hydrochloric acid. W. Guertler and T. Liepus observed no reaction with 10 and 50 per cent. soln. of **sodium sulphide**—with or without alkali. N. Domanicky observed that an ethereal soln. of **sulphur monochloride** readily attacks molybdenum. According to E. F. Smith and V. Oberholtzer, if molybdenum is heated in the vapour of sulphur monochloride, a complex $Mo_5S_8Cl_9$ is formed. L. Storch found that the presence of sulphomolybdates prevents the precipitation of copper, cadmium, mercury, and iron sulphides.

C. H. Ehrenfeld said that when the metal is heated in **sulphur dioxide,** molybdenum dioxide and a sublimate of sulphur are formed ; whilst J. Férée observed that with pyrophoric molybdenum and sulphur dioxide, the mass glows and a sulphide and oxide are formed. According to J. J. Berzelius, and C. F. Bucholz, dil. **sulphuric acid** does not act on molybdenum, whilst the hot, conc. acid forms sulphur dioxide and molybdenum dioxide if only a small proportion of acid be present, with more acid, blue molybdenum oxide is formed. W. Lederer said that dil. and conc. sulphuric acid do not attack molybdenum ; but A. Rosenheim and H. J. Braun added that molybdenum is attacked only slowly by dil. sulphuric acid, whilst the conc. acid quickly forms a bluish-green soln. According to W. Muthmann, an excess of conc. sulphuric acid begins to act feebly on molybdenum at 160° and sulphur dioxide is evolved ; the grass-green liquid darkens to an olive-green. If the temp. is not too high, all the metal dissolves. If the temp. is near the b.p. of the acid, the soln. becomes blue and then colourless—the dioxide first formed is oxidized to molybdenum trioxide. W. E. Ruder found that sulphuric acid of sp. gr. 1·30 does not attack molybdenum at 110° ; but that the conc. acid of sp. gr. 1·82 attacks it slowly. Only 0·29 per cent. loss in weight was found after 18 hrs. With elevated temp., however (200°–250°), the metal dissolves rapidly to a green soln., with the evolution of sulphur dioxide. W. Rohn noted that 10 per cent. cold sulphuric acid dissolved 9·006 per cent. after 24 hrs., and only 0·0015 per cent. dissolved in the hot acid in an hour, and 0·03 per cent. in 24 hrs. R. H. Adie added that the reaction with conc. sulphuric acid begins with the evolution of gas at 115° ; sulphur dioxide is given off at 135°, and no hydrogen sulphide. A green solid is formed. W. Guertler and T. Liepus found that 10 per cent. sulphuric acid does not attack chromium during 48 hrs.' exposure ; and similarly with 20 per cent. H_2SO_4 sat. with sodium sulphate. C. G. Fink found that fused **potassium hydrosulphate** readily attacks the metal.

A. Vandenberghe observed no reaction between molybdenum and **nitrogen ;** I. Zschukoff said there is a slight reaction at 1000°, and H. Moissan added that no combination occurs at 1200° ; whilst J. Ferée found no combination with gently-heated, pyrophoric molybdenum in nitrogen. E. Martin studied the occlusion of nitrogen, and the formation of nitrides, by the metal. I. Langmuir observed that when a molybdenum filament is heated to 2000° or 2400° in nitrogen at 0·3 mm. press., the nitrogen is all absorbed. N. R. Campbell made some observations on this subject. E. J. B. Willey measured the rate of decay of active nitrogen in the presence of a molybdenum filament. The phenomenon is discussed in connection with molybdenum nitride—**8**. 49, 12. E. F. Smith and V. Oberholtzer found that **ammonia** has no action on molybdenum at temp. up to a red-heat. The action at high temp. was studied by C. H. Kunsman ; E. S. Lamer and W. E. Deming, and C. H. Kunsman and co-workers discussed the catalytic effect of molybdenum on the decomposition of ammonia. W. Guertler and T. Liepus observed no reaction during 8 hrs.' exposure to 10, 50, and 70 per cent. aq. ammonia ; but C. Matignon and G. Desplantes observed that when shaken up at ordinary temp. in a flask containing 10 c.c. of aq. ammonia (1 : 4), molybdenum is oxidized ; C. H. Ehrenfeld, that **methylamine** is also inactive—the trace of hydrogen cyanide which is formed is due to the decomposition of the amine ; and F. W. Bergstrom found that a soln. of **potassamide** in liquid ammonia acts very slowly or not at all. According to C. H. Ehrenfeld, when molybdenum is heated in **nitrous oxide,** it forms molybdenum trioxide ; and likewise also with **nitric oxide.** F. Emich said that with finely-divided molybdenum in nitric oxide, at the beginning of a red-heat, there are formed successively MoO_2, Mo_2O_3, Mo_5O_{12}, and finally MoO_3. C. H. Ehrenfeld also observed that in **nitrogen peroxide,** molybdenum trioxide is formed. J. Férée found that pyrophoric molybdenum glows in nitrogen peroxide, forming oxide and nitride. J. J. Berzelius, and C. F. Buchloz observed that **nitric acid** attacks molybdenum with the development of nitrous fumes ; with a large proportion of acid molybdenum trioxide is formed ; with less acid, the dioxide. W. Lederer said that dil. nitric acid does not attack the metal immediately in the cold, but with the hot acid, the liquid is coloured yellow, brown, and blue, and a protective layer of molybdenum trioxide forms on the metal; with conc. nitric acid this layer is formed at once—*vide supra,* passive molybdenum. C. Montemartini observed that molybdenum is attacked by 3 to 70 per cent. acid without the formation of ammonia. Conc. acid (70 per cent.) attacks the metal but slowly; a much more vigorous action occurs with a less conc. acid (50 per cent.), and a reddish soln. and residue are obtained. The soln. reduces permanganate, so that the metal is not immediately converted into molybdenum trioxide by 50 per cent. acid, but a nitrate is first formed; 70 per cent. acid at once gives molybdenum trioxide. The quantity of nitric oxide produced in the reaction between nitric acid and molybdenum decreases as the conc. of the acid increases; nitric peroxide is the main gaseous product with 50 per cent. acid. Neither nitrogen nor nitrous oxide is formed. W. Guertler and T. Liepus found that 10 and 50 per cent. HNO_3 have no action on molybdenum in 8 hrs., and similarly with aqua regia. W. E. Ruder said that conc. nitric acid of sp. gr. 1·40 dissolves molybdenum slowly forming molybdenum trioxide, which deposits on the surface of the metal and retards the action; but a more dil. acid of sp. gr. 1·15 attacks the metal rapidly. Aqua regia dissolves the metal rapidly, particularly when hot. W. Rohn added that 10 per cent. nitric acid in the cold dissolved 5·2 per cent. in 24 hrs., and the hot acid, 1·8 per cent. in one hour. J. J. Berzelius, C. F. Bucholz, H. Moissan, and W. Lederer found that mixtures of sulphuric, hydrofluoric, or hydrochloric acid with nitric acid quickly attack molybdenum. L. Marino, and W. E. Ruder said that molybdenum is rapidly attacked by hot aqua regia. F. W. Bergstrom found that the metal is slightly attacked by a soln. of ammonium nitrate. W. Lederer, C. G. Fink, and H. Moissan found that fused **potassium nitrate** oxidizes molybdenum rapidly though less violently than the fused chlorate; and similarly with **sodium nitrate.** Purified molybdenum does not unite with **phosphorus** at the m.p. of glass. When the metal is gently heated with **phosphorus pentachloride,** a volatile chloride is formed which rapidly acquires a blue colour when exposed to moist air. Most molybdenum compounds give this reaction and therefore it may be used as a test for molybdenum. W. Rohn found that a cold 10 per cent. of **phosphoric acid** dissolved 0·03 per cent. of molybdenum in 24 hrs., and the hot acid, 0·009 per cent. in one hour. W. Guertler and H. Schack found that if a rod of molybdenum be placed in a mass of fused **antimony trisulphide,** it dissolves to the disulphide liberating an eq. quantity of antimony.

H. Moissan observed that when a mixture of molybdenum and **boron** is heated in the electric furnace, a crystalline boride is formed; and **silicon,** under similar conditions, furnishes a crystalline silicide. When the metal is heated with **carbon** at about 1500°, it undergoes cementation, and becomes hard enough to scratch glass, and if heated at 300° and suddenly cooled in water, it becomes brittle and will still scratch glass. If carboniferous molybdenum is heated with the dioxide, at a temp. much below its m.p., the carbon is removed. The phenomenon is said to be connected with the volatility of the oxide. The reaction with carbon was also studied by G. Tammann and K. Schönert, A. Westgren and G. Phragmen, T. Takei, and K. Nischk—*vide* carbides. W. Lederer also observed that molybdenum becomes harder when heated with carbon, and that gaseous **hydrocarbons** are decomposed with the separation of carbon. S. Hilpert and M. Ornstein found that the carbide is formed when the powdered metal is heated at 600°–1000° in a mixture of hydrogen and **methane** (1 : 1); E. F. Smith and V. Oberholtzer found that **carbon monoxide** has no action on molybdenum at a red-heat; but S. Hilpert and M. Ornstein obtained the carbide Mo_2C by heating the powdered metal in an atm. of carbon monoxide, and J. Férée found that carbon monoxide acts on pyrophoric molybdenum with a slight rise of temp., and a sudden glowing of the metal with the absorption of oxygen and the separation of carbon. A. Vandenberghe observed that molybdenum (and its lower oxides) reduces **carbon dioxide,** forming carbon monoxide; the reaction is reversible: $Mo+3CO_2 \rightleftharpoons 3CO+MoO_3$, since, under suitable conditions, the trioxide is reduced to the metal by carbon monoxide. J. Férée found that pyrophoric molybdenum at ordinary temp. acts on carbon dioxide with a slight rise of temp. W. Guertler and T. Liepus observed no action on molybdenum by water sat. with carbon dioxide during 8 hrs.' exposure. S. Medsforth studied the action of molybdenum on the nickel catalyst in the hydrogenation of carbon monoxide or dioxide; and A. Korczynsky, in reactions with organic compounds. E. F. Smith and V. Oberholtzer observed that at 150° to 200°, **carbonyl chloride** forms a liquid sublimate which yields a gelatinous mass on cooling —it is a mixture of $MoOCl_4$ and $Mo(CO)Cl_4$. C. Beindl used molybdenum as catalyst in the synthesis of hydrocyanic acid from nitrogen, hydrogen, and carbon monoxide; and O. Schmidt, and R. Hocart, as a hydrogenation catalyst. W. Guertler and T. Liepus observed no reaction during 48 hrs.' exposure of the metal to soln. of **citric acid** and **tartaric acid.** E. W. Engle said that molybdenum is markedly attacked by the weaker organic acids. W. Rohn added that after 24 hrs.' action by cold 10 per cent. **acetic acid,** 0·02 per cent. of metal was dissolved; whilst 0·003 per cent. dissolved in the hot acid in an hour.

The alloys of molybdenum with the **metals** are discussed below. J. J. Berzelius, and C. F. Bucholz found that a boiling soln. of **potassium hydroxide** does not oxidize molybdenum; whilst the fused hydroxide slowly attacks the metal, and, according to J. von Liebig, converts it into the trioxide. W. Guertler and T. Liepus observed no reaction with less than 8 hrs.' exposure to 10 and 50 per cent. NaOH. H. Kuessner found that molybdenum goes into soln. anodically in N-KOH as sexivalent molybdenum, and at low temp. some oxygen is evolved. W. E. Ruder observed no action by soln. of potassium hydroxide, but the metal is soluble in the fused alkali. M. Leblanc and O. Weyl observed that between 550° and 660° fused potassium hydroxide has a slight action on fused potassium hydroxide, forming traces of potassium and hydrogen.

E. F. Smith and co-workers observed that molybdenum precipitates copper incompletely from soln. of **copper salts.** According to H. Moissan, **silver fluoride** reacts with molybdenum without forming volatile products. J. S. de Benneville observed that molybdenum dissolves in a soln. of **silver nitrate** with the separation of silver, and, added E. F. Smith and co-workers, the soln. becomes turbid owing to the separation of molybdic acid. The turbidity is not produced with an ammoniacal soln. of silver oxide or chloride. The reaction is quantitative, one gram-atom of molybdenum precipitates six gram-atoms of silver. Hence, in the case of chloride, the dark brown soln. must contain molybdenum hexachloride. This is also formed with a soln. of **gold chloride,** for a gram-atom of molybdenum precipitates two gram-atoms of gold. H. Moissan found that solid **zinc fluoride** reacts with molybdenum without forming a volatile product. According to E. F. Smith and co-workers, soln. of **cadmium salts** are not affected by molybdenum. Molybdenum reduces a neutral soln. of **mercuric chloride** to mercurous chloride and eventually to mercury. W. Guertler and T. Liepus observed that a 1 : 500 mercuric chloride soln. at 90° is stable with molybdenum; whilst a **magnesium chloride** soln. does not attack the metal in 8 hrs. H. Moissan observed that the reaction with **lead fluoride** resembles that with silver fluoride. E. F. Smith and co-workers observed no reaction with acidic, neutral, or alkaline soln. of **lead salts;** nor is there any reaction with **bismuth salts.** E. F. Smith and H. C. Burr, and C. H. Ehrenfeld found that molybdenum reduces **ferric chloride** to the ferrous salt, and from the amount of iron reduced it follows that the molybdenum forms the hexachloride. E. F. Smith observed a partial reduction to metal with soln. of **platinum, palladium,** and **rhodium salts.**

Some reactions of analytical interest.—General observations on the analysis of mixtures containing molybdenum were made by A. A. Noyes and W. C. Bray,[2] and E. Knoevenagel and E. Ebler. A conc. soln. of an alkali molybdate gives a white precipitate when treated with **dilute acids.** The precipitate is soluble in excess. According to F. von Kobell,[3] O. Maschke, and L. Schönn, if a trace of a molybdenum salt mixed with conc. **sulphuric acid** is evaporated nearly to dryness the mass is coloured intensely blue. If antimony or tin be present, the mixture should be first evaporated to dryness with phosphoric acid before heating it with sulphuric acid. P. Truchot added that if vanadic acid be present, a green colour may be produced. If the molybdenum soln. be treated with **hydrogen sulphide,** the liquid becomes blue, and molybdenum trisulphide is gradually precipitated as a brownish-black solid which forms a brown soln. with alkali or ammonium sulphide. The trisulphide is reprecipitated by acids. The molybdenum sulphide is oxidized by hot sulphuric or nitric acid, or by roasting in air, to white molybdenum trioxide. Molybdenum sulphide is not attacked by a soln. of oxalic acid whereas tin sulphide is dissolved. Hydrogen and ammonium sulphides act similarly on salts of the lower oxides; and, it might be added, the salts of the lower oxides furnish precipitates with **alkali hydroxides and carbonates** which are soluble in an excess of the carbonate soln. As shown by E. Dohler,[4] E. H. Miller, etc., the precipitation of molybdenum as sulphide from acidic soln. by hydrogen sulphide atm. press. is imperfect. If the soln. be sat. with hydrogen sulphide and heated in a sealed bottle on a water-bath, the precipitation is complete. If a soln. of a molybdate be treated with a **reducing agent**—*e.g.*, zinc and hydrochloric or sulphuric acid, stannous chloride, mercurous nitrate, ferrous sulphate, sodium hypophosphite, sulphur dioxide, etc.—the liquid is coloured blue, then green, and finally brown. L. A. Munro found that the reaction when used as a test for tin in stannous chloride is sensitive to 1 : 1,423,000. According to E. Kafka,[5] if to the neutral soln. of either compound is added a drop of sat. soln. of mercurous nitrate, then 1 c.c. of conc. hydrochloric acid, and further an excess of potassium iodide, a precipitate of mercurous iodide will form and redissolve, mercury will deposit, and the supernatant liquid will gradually turn blue—very dil. soln. of molybdic acid are, however, not affected. To distinguish between tungsten and molybdenum, potassium thiocyanate is added, when in the case of molybdenum the blue colour will change to blood-red. If **potassium thiocyanate** be added to an acidic soln. of a molybdenum salt, there is no perceptible change, but if the soln. be then treated with zinc, stannous chloride soln. or hydrogen sulphide,[6] a blood-red coloration appears. Unlike the case with iron, this coloration occurs in the presence of phosphoric acid. The presence of tartaric and other organic acids hinders the reaction. If the red soln. be shaken with ether, the coloured compound passes from the aq. to the ethereal layer. A few drops of a soln. of **sodium phosphate** added to a nitric acid soln. of a molybdate slowly furnishes a yellow precipitate of ammonium phosphomolybdate. The precipitation occurs more quickly with hot soln. Arsenates produce an analogous precipitation. Salts of the lower oxides also give precipitates with alkali phosphate. According to M. Siewert, molybdenum compounds give a red or plum coloured reaction with **xanthic acid.** S. L. Malowan recommended applying the test as follows: Absolute alcoholic potash is shaken with excess of carbon disulphide until no more of the latter is dissolved. To the soln. so obtained, 30 per cent. acetic acid is added until it shows a slight yellow turbidity, and the reagent is added drop by drop to the soln. to be tested. If molybdenum is present, an intense red colour develops, which is quite stable in water, and the intensity of which is proportional to the quantity of molybdenum present. The sensitiveness of the reaction is such that 0·000005 grm. of molybdenum in 0·0007 per cent. soln. can be detected with certainty in presence of other elements. The coloured product is readily soluble in ethyl or amyl alcohol, ether, or chloroform. less easily in petroleum and benzene. It is readily extracted from its reddish-violet ethereal soln. by alkalies, from which acids precipitate it. The ethereal soln. decomposes on keeping, with formation of molybdenum sulphide. The reaction is not given by vanadium, tungsten, titanium, or uranium; chromates give a dark coloration with xanthic acid, and should be reduced, if present, before the test is made. The reaction can be used for the colorimetric estimation of molybdenum, the coloured product being extracted with a mixture of 65 per cent. ether and 35 per cent. light petroleum, and a mixture of 30 per cent. ether and 70 per cent. light petroleum used for dilution for comparison with the standard soln. If pure ether is used, decomposition takes place too rapidly for accurate determinations to be made. The process was studied by J. Koppel,[7] and D. Hall. Neutral soln. of molybdates give with **mercurous nitrate** a white precipitate soluble in nitric acid ; **lead acetate** precipitates white lead molybdate soluble in nitric acid ; **potassium ferroycanide,** in a soln. acidified with hydrochloric acid, gives a reddish-brown precipitate. Salts of the lower oxides also give precipitates with potassium ferrocyanide and ferricyanide. E. Lecocq obtained an indigo-violet coloration with an alcoholic soln. of **diphenylcarbazide ;** L. Spiegel and T. A. Maass, and M. E. Pozzi-Escot, a wine-red coloration with an acetic acid soln. of **phenylhydrazine ;** L. Lévy observed a number of colour reactions with **alkaloids ;** E. Kedesdy, and M. E. Pozzi-Escot, a brown colour with **tannin ;** and many other colour reactions with organic substances have been reported. F. Steidler studied the colours produced by molybdenum salts on **silk** dipped in turmeric or α-nitroso-β-naphthol with a view to the microdetection of the element. J. H. Muller [8] found that **salicylic acid** gives a yellow coloration but no precipitate with soln. of the alkali molybdates. H. J. H. Fenton observed a red or brown colour is produced by molybdates and **dihydroxymaleic acid**; and J. H. de Boer, a violet coloration with **alizarinsulphonic acid.** Like titanic acid soln., molybdates give a yellowish colour with **hydrogen dioxide.**

Some uses of molybdenum.—Several patents have been taken for the use of molybdenum filaments in the incandescent lamp industry.[9] The Gebrüder Siemens u. Co. used molybdenum as an ingredient in the preparation of arc-light electrodes. Preparations of molybdenum have been recommended in photographic work ;[10] in dyeing [11] silks, woollens, and leather,[12] and rubber ; in the preparation of blue colours,[13] and for producing red and yellow pottery glazes and glasses [14] for colouring artificial emeralds ;[15] and as a catalytic agent in chemical operations [16] molybdic acid has been tried as a depolarizing agent in place of nitric acid ;[17] various compounds are used as chemical reagents ; and as a preservative for smokeless powder in hot climates.[18] Molybdenum trisulphide has been recommended as a solder for lamp-filaments.[19] Molybdenite is used as a rectifier in wireless telegraphy. Molybdenum wire has been recommended as resistance wire in electric furnaces.[20] It is used as a substitute for platinum and platinum-iridium alloys [21] in various make-and-break contact devices ; in dentistry ; in the manufacture of X-ray tubes ; and as a wire for supporting the filaments of incandescent lamps,[22] and as a support for refractory materials.[23] The most important application of molybdenum is in the preparation of alloys, and particularly of special steels—molybdenum steels. When compared with other alloy-steels, and tempered by heat to the same tensile strength, A. H. Hunter [24] said that molybdenum steels have a slightly higher elastic limit, and elastic ratio ; a higher elongation or greater ductility ; and a higher reduction of area or greater toughness. The molybdenum steels are used for motor-car frames, shafts, and rods for motor-cars, and aeroplanes ; high-pressure boiler-plates, linings for big-guns ; rifle barrels ; armour plate and armour-piercing projectiles ; steel-balls for grinding mills ; permanent magnets ; etc.

REFERENCES.

[1] A. Vandenberghe, *Zeit. anorg. Chem.*, **11**. 397, 1896 ; A. Rosenheim and H. J. Braun, *ib.*, **46**. 311, 1905 ; A. Westgren and G. Phragmen, *ib.*, **156**. 27, 1926 ; C. H. Kunsman, *Journ. Amer. Chem. Soc.*, **50**. 2110, 1928 ; J. A. Hedvall and N. von Zweigbergk, *ib.*, **108**. 119, 1919 ; G. Tammann and K. Schönert, *ib.*, **122**. 27, 1922 ; E. Siedschlag, *ib.*, **131**. 191, 1923 ; F. Emich, *Monatsh.*, **15**. 375, 1894 ; L. Hamburger, *Chem. Weekly*, **13**. 2, 1916 ; R. H. Adie, *Proc. Chem. Soc.*, **15**. 133, 1899 ; *Chem. News*, **79**. 261, 1899 ; A. Korczynsky, *Bull. Soc. Chim.*, (4), **29**. 283, 1921 ; W. Lederer, *Darstellung und Untersuchung reinen, geschmolzen Molybdäns*, Erlangen, 14, 1911 ; F. Fischer and F. Schrötter, *Ber.*, **43**. 1442, 1454, 1910 ; J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817 ; *Ann. Chim. Phys.*, (2), **17**. 5, 1921 ; *Pogg. Ann.*, **4**. 153, 1825 ; **6**. 331, 369, 1826 ; **7**. 261, 1826 ; C. F. Bucholz, *Svenska Akad. Handl.*, 145, 1825 ; *Scherer's Journ.*, **9**, 485, 1803 ; *Gehlen's Journ.*, **4**. 598, 1803 ; *Phil. Mag.*, **16**. 193, 1803 ; *Nicholson's Journ.*, **20**. 121, 188, 253,

1808 ; *Journ. Mines*, **18**. 241, 1808 ; C. G. Fink, *Chem. News*, **104**. 34, 1910 ; *Trans. Amer. Electrochem. Soc.*, **17**. 232, 1910 ; **22**. 499, 1912 ; *Chem. Eng.*, **12**. 51, 1910 ; *Met. Chem. Engg.*, **8**. 341, 1910 ; *Chem. News*, **104**. 34, 1911 ; J. Férée, *Compt. Rend.*, **122**. 733, 1896 ; H. Moissan, *ib.*, **120**. 1230, 1895 ; *Bull. Soc. Chim.*, (3), **13**. 966, 1895 ; (3), **15**. 1282, 1896 ; *Ann. Chim. Phys.*, (7), **9**. 337, 1896 ; *Bull. Soc. Enc. Nat. Ind.*, **101**. ii, 232, 1902 ; *Compt. Rend.*, **122**. 1302, 1896 ; J. A. Kendall, *Proc. Roy. Soc.*, **36**. 208, 1884 ; *Chem. News*, **49**. 49, 1884 ; L. J. Thénard, *Traité de chimie*, Paris, **2**. 68, 1824 ; M. Guichard, *Compt. Rend.*, **131**. 998, 1900 ; C. Matignon and G. Desplantes, *ib.*, **140**. 853, 1905 ; G. Chaudron, *ib.*, **170**. 182, 1920 ; *Études des réactions réversibles de l'hydrogène et l'oyxde de carbone sur les oxydes n étalliques*, Paris, 1921 ; E. Martin, *Arch. Eisenhüttenwesen*, **3**. 407, 1929 ; *Stahl Eisen*, **49**. 1861, 1920 ; *Ein Beitrag zur Frage der Aufnahmefähigkeit des reinen Eisens und einiger seiner Leigierungselemente für Wasserstoff und Stickstoff*, Düsseldorf, 1929 ; N. B. Pilling and R. E. Bedworth, *Chem. Trade Journ.*, **72**. 317, 1923 ; *Chem. Met. Engg.*, **27**. 72, 1922 ; *Metal Ind.*, **22**. 560, 586, 619, 1923 ; *Journ. Inst. Metals*, **29**. 529, 1923 ; L. Storch, *Ber.*, **16**. 2015, 1883 ; O. Schmidt, *Zeit. phys. Chem.*, **118**. 193, 1925 ; H. V. Regnault, *Ann. Chim. Phys.*, (2), **62**. 337, 1836 ; C. Beindl, *U.S. Pat. No.* 1492193, 1492194, 1924 ; C. W. Blomstrand, *Journ. prakt. Chem.*, (1), **77**. 89, 1859 ; (1), **82**. 436, 1861 ; C. Montemartini, *Gazz. Chim. Ital.*, **22**. i, 384, 1892 ; L. Marino, *ib.*, **35**. ii, 193, 1905 ; W. E. Ruder, *Journ. Amer. Chem. Soc.*, **34**. 387, 1912 ; J. H. Müller, *ib.*, **37**. 2053, 1915 ; C. H. Ehrenfeld, *ib.*, **17**. 381, 1895 ; J. S. de Benneville, *ib.*, **16**. 735, 1894 ; I. Langmuir, *ib.*, **41**. 167, 1919 ; E. F. Smith and H. C. Burr, *ib.*, **16**. 577, 1894 ; E. F. Smith and V. Oberholtzer, *ib.*, **15**. 206, 1923 ; *Zeit. anorg. Chem.*, **5**. 63, 1893 ; I. Zschukoff, *Ann. Inst. Anal. Phys. Chim.*, **3**. 14, 1926 ; S. Hilpert and M. Ornstein, *Ber.*, **46**. 1669, 1913 ; M. Leblanc and O. Weyl, *ib.*, **45**. 2300, 1912 ; K. Nischk, *Zeit. Elektrochem.*, **29**. 373, 1923 ; H. Kuessner, *ib.*, **16**. 754, 1910 ; F. R. Michel, *Ueber krystallisierte Verbindungen des Aluminiums mit Metallen*, Göttingen, 1860 ; E. J. B. Willey, *Journ. Chem. Soc.*, 2188, 1927 ; W. Guertler, *Zeit. Metallkunde*, **15**. 150, 251, 1923 ; W. Guertler and H. Schack, *Metall Erz*, **20**. 361, 426, 1923 ; W. Guertler and T. Liepus, *Zeit. Metallkunde*, **17**. 310, 1925 ; W. Rohn, *ib.*, **18**. 387, 1926 ; J. von Liebig, *Kastner's Arch.*, **2**. 57, 1824 ; N. Domanicky, *Journ. Russ. Phys. Chem. Soc.*, **48**. 1724, 1916 ; S. Medsforth, *Journ. Chem. Soc.*, **123**. 1452, 1923 ; L. O. Bannister, *ib.*, 3163, 1928 ; *Metal Ind.*, **35**, 27, 1929 ; E. W. Engle, *Trans. Amer. Inst. Min. Eng.*, **71**. 691, 1925 ; F. W. Bergstrom, *Journ. Phys. Chem.*, **29**. 160, 1925 ; N. R. Campbell, *Phil. Mag.*, (7), **2**. 369, 1926 ; R. Hocart, *Bull. Soc. Chim.*, (4), **39**. 398, 1926 ; W. Muthmann, *Liebig's Ann.*, **238**. 108, 1887 ; W. G. Mixter, *Amer. Journ. Science*, (4), **29**. 488, 1910 ; T. Takei, *Science Rep. Tohoku Univ.*, **17**. 929, 1928 ; C. H. Kunsman, E. S. Lamar and W. E. Deming, *Phil. Mag.*, (7), **10**. 1015, 1930 ; E. S. Lamar and W. E. Deming, *ib.*, (7), **9**. 28, 1930 ; O. Ruff and H. Krug, *Zeit. anorg. Chem.*, **190**. 270, 1930.

[2] A. A. Noyes and W. C. Bray, *Journ. Amer. Chem. Soc.*, **29**. 137, 1907 ; *Chem. News*, **93**. 134, 1906 ; G. Pohl, *Beiträge zur Kenntnis einiger Verbindungen des Molybdäns und deren Untersuchung*, Bern, 1906 ; E. Knoevenagel and E. Ebler, *Ber.*, **35**. 3055, 1902.

[3] F. von Kobell, *Charakteristik der Mineralien*, Nürnberg, 109, 1031 ; *Grundzüge der Mineralogie*, Nürnberg, 284, 1838 ; *Zeit. anal. Chem.*, **14**. 317, 1875 ; O. Maschke, *ib.*, **12**. 280, 1873 ; *Arch. Pharm.*, (3), **6**. 125, 1874 ; L. Schönn, *Zeit. Chem.*, (2), **6**. 282, 1870 ; *Zeit. anal. Chem.*, **8**. 379, 1869 ; **9**. 41, 311, 1870 ; P. Truchot, *Ann. Chim. Anal.*, **10**. 254, 1905.

[4] E. Dohler, *Chem. Ztg.*, **24**. 537, 1900 ; *Chem. News*, **82**. 292, 1900 ; E. H. Miller, *ib.*, **90**. 204, 218, 1904 ; *Journ. Amer. Chem. Soc.*, **26**. 675, 1904 ; L. Dede and T. Becker, *Zeit. anorg. Chem.*, **152**. 185, 1926 ; L. Moser and M. Behr, *ib.*, **133**. 67, 1924 ; K. Wendehorst, *ib.*, **144**. 319, 1925 ; F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie, Leipzig*, **2**. 183, 1911 ; B. Herstein, *Bull. U.S. Agric. Chem. Dept.*, 150, 1912 ; J. W. Mellor, *A Treatise on Quantitative Inorganic Analysis*, London, 411, 1913 ; L. A. Munro, *Proc. Nova Scotia Inst.*, **16**. 9,19 27.

[5] R. Namias, *Gazz. Chim. Ital.*, **21**. ii, 361, 1891 ; E. Kafka, *Zeit. anal. Chem.*, **51**. 482, 1912 ; M. E. Pozzi-Escot, *Bull. Soc. Chim.*, (4), **13**. 402, 1042, 1913 ; E. J. Millard, *Pharm. Journ.*, (3), **19**. 585, 1889.

[6] D. Ganassini, *Boll. Chim. Farm.*, **41**. 417, 1902 ; M. Siewert, *Zeit. ges. Naturwiss*, **4**. 23, 1864 ; S. L. Malowan, *Zeit. anorg. Chem.*, **108**. 73, 1919.

[7] E. J. Millard, *Pharm. Journ.*, (3), **19**. 585, 1889 ; E. Lecocq, *Bull. Assoc. Belg. Chem.*, **17**. 412, 1903 ; M. E. Pozzi-Escot, *Ann. Chim. Anal.*, **12**. 92, 1907 ; L. Lévy, *Compt. Rend.*, **103**. 1074, 1195, *Ann. Chim. Phys.*, (6), **25**. 433, 1892 ; *Chem. News*, **54**. 300, 1886 ; H. J. H. Fenton, *Journ. Chem. Soc.*, **93**. 1064, 1908 ; L. Spiegel and T. A. Maass, *Ber.*, **36**. 512, 1903 ; E. Kedesdy, *Mitt. Materialprüf. Amt.*, **25**. 268, 1908 ; F. Steidler, *Mikrochemie*, **2**. 131, 1924 ; J. Koppel, *Chem. Ztg.*, **43**. 777, 1919 ; D. Hall, *Journ. Amer. Chem. Soc.*, **46**. 1462, 1922.

[8] L. Schönn, *Dingler's Journ.*, **210**. 317, 1873 ; *Zeit. anal. Chem.*, **9**. 311, 1870 ; J. H. de Boer, *Chem. Weekbl.*, **21**. 404, 1924 ; A. Weller, *Ber.*, **15**. 2592, 1882 ; C. Bärwald, *ib.*, **17**. 1206, 1885 ; *Beiträge zur Kenntniss Molybdäns*, Berlin, 1885 ; G. Werther, *Journ. prakt. Chem.*, (1), **83**. 195, 1861 ; *Arch. Sciences Genève*, (2), **11**. 82, 1861 ; L. Crismer, *Gaz. Méd. Liège*, 77, 1888 ; *Bull. Soc. Chim.*, (3), **6**. 22, 1891 ; G. Denigès, *ib.*, (3), **3**. 797, 1890 ; (3), **5**. 293, 1891 ; (3), **6**. 22, 1891 ; *Compt. Rend.*, **110**. 1007, 1890 ; E. Péchard, *ib.*, **112**. 720, 1891 ; **114**. 1481, 1892 ; A. C. Stark, *Pharm. Journ.*, (3), **23**. 757, 1893 ; J. H. Muller, *Journ. Amer. Chem. Soc.*, **33**. 1506, 1911 ; D. Hall, *ib.*, **44**. 1462, 1922 ; H. J. H. Fenton, *Journ. Chem. Soc.*, **93**. 1064, 1908 ; S. L. Malowan, *Zeit. anorg. Chem.*, **108**. 73, 1919 ; J. Koppel, *Chem. Ztg.*, **43**. 777, 1919 ; M. Siewert, *Zeit. ges. Naturwiss.*, **4**. 23, 1864.

[9] Wolfram Lampen A. G., *German Pat.*, *D.R.P.* 184379, 1905 ; 191, 883, 198466, 1906 ;

209349, 1908; 237014, 1910; Deutsche Gasgluhlicht A. G., *ib.*, 194653, 1905; A. Just and F. Hanaman, *ib.*, 154262, 1903; H. Kuzel, *ib.*, 192290, 1905; 194348, 194707, 1905; J. Lux, *ib.*, 193920, 1905; 194171, 194894, 1906; 210325, 212104, 212962, 216903, 1906; F. J. Planchon, *ib.*, 194896, 1907; Allgemeine Elektrizitäts Gesellschaft, *ib.*, 207395, 1907; Gebrüder Siemens u. Co., *ib.*, 216800, 1908; L. Moser, *Oesterr. Chem. Ztg.*, **26**. 67, 1923; A. Lottermoser, *Chem. Ztg.*, **32**. 311, 1908; H. Alterthum, *Zeit. angew. Chem.*, **42**. 2, 1929.

[10] R. E. Liesegang, *Phot. Arch.*, **36**. 282, 1895; G. H. Nievenglowsky, *Jahrb. Phot.*, **9**. 24, 1895; R. Namias, *Monit. Scient.*, (4), **19**. 106, 1905; Neue Photographische Gesellschaft, *German Pat., D.R.P.* 206320, 1907.

[11] Société Scheurer et Lanth, *Monit. Scient.*, (4), **10**. 189, 1896; *French Pat. No.* 253741, 1897; F. W. Schmidt, *German Pat., D.R.P.* 68417, 69410, 1892.

[12] M. E. Pozzi-Escot, *Compt. Rend.*, **135**. 880, 1902.

[13] R. Zsigmondy, *Dingler's Journ.*, **273**. 29, 1889.

[14] P. Hautefeuille and A. Perrey, *Compt. Rend.*, **106**. 1800, 1888.

[15] O. Wichardt, *German Pat., D.R.P.* 167122, 1904; W. H. von Kurrer, *Dingler's Journ.*, **129**. 139, 1853; R. Wagner, *ib.*, **205**. 386, 1878; *Wagner's Jahresb.*, **17**. 759, 1871; A. W. Hoffmann, *Berichte über die chemische Industrie*, Braunschweig, **1**. 1018, 1875.

[16] J. Reich, *Elektrolytische Reduktion von Nitrokörpern mit Molybdän als Wasserstoffüberträger*, München, 1910; Badische Anilin- und Sodafabrik, *German Pat. D.R.P.*, 246377, 1910; Kinzlberger u. Co., *ib.*, 228664, 1908; *Zeit. Elektrochem.*, **15**. 765, 1909; A. Kurtenacker, *Zeit. anal. Chem.*, **50**. 548, 1911; H. W. Underwood, *Chem. Met. Engg.*, **29**. 709, 1923; C. Beindl, *U.S. Pat. No.*, 1492193, 1492194, 1924.

[17] C. T. Oppermann, *German Pat., D.R.P.* 75840, 1893; *Zeit. Elektrochem.*, **1**. 62, 1895.

[18] R. H. Rastall, *Molybdenum Ores*, London, 11, 1920.

[19] C. H. Weber, *German Pat., D.R.P.* 231330, 1910.

[20] R. Winne and C. Dantsizen, *Met. Chem. Engg.*, **9**. 537, 1911; W. E. Ruder, *Trans. Amer. Inst. Min. Eng.*, **59**. 162, 1918; E. W. Engle, *ib.*, **71**. 691, 1925; H. J. Miller and M. Linderman, *ib.*, 13, 1927; J. and W. B. Mitchell, *Trans. Cer. Soc.*, **25**. 39, 1926; P. Fleury, *Compt. Rend.*, **175**. 880, 1922; *Journ. Franklin Inst.*, **195**. 425, 1923; P. W. Döhmer, *Zeit. Ver. deut. Ing.*, **72**. 556, 1928; C. M. Thompson, *Iron Steel Eng.*, **7**. 471, 1930; W. D. Coolidge, *Journ. Ind. Eng. Chem.*, **4**. 2, 1912.

[21] F. A. Fahrenwald, *Trans. Amer. Inst. Min. Eng.*, **54**. 541, 1916.

[22] W. D. Coolidge, *Journ. Ind. Eng. Chem.*, **4**. 2, 1912.

[23] J. H. Härden, *Chem. Met. Engg.*, **33**. 543, 1926.

[24] A. H. Hunter, *Blast Furnace*, **9**. 356, 426, 1921; *Iron Age*, **107**. 1469, 1511, 1921; *Year Book Amer. Iron Steel Inst.*, 127, 1921; *Metal Ind.*, **19**. 157, 1921; N. W. Bratton, *Eng. Min. Journ.*, **111**. 148, 1921; W. E. Simpson, *Min. Scient. Press.*, **119**. 894, 1919; M. H. Schmid, *Chem. Met. Engg.*, **24**. 927, 1921; *Trans. Amer. Soc. Steel Treating*, **1**. 500, 1921; J. O. Arnold and F. Ibbotson, *Journ. Iron Steel Inst.*, **99**. i, 407, 1919; J. M. Gledhill, *ib.*, **66**. ii, 127, 1904; T. Swinden, *Carnegie Mem. Iron Steel Inst.*, **3**. 66, 1911; **5**. 100, 1913; H. D. Hibbard, *Bull. U.S. Bur. Mines*, 100, 1915; P. Powell, *Brass World*, **20**. 117, 1924; R. Cazaud, *Aciers speciaux*, **4**. 590, 1929.

§ 6. The Atomic Weight and Valency of Molybdenum

The valency of molybdenum has been discussed by H. Kauffmann.[1] In many ways the valency of molybdenum is analogous with that of chromium. The element appears to be *bivalent* in the dichloride, but, according to W. Muthmann and W. Nagel, this valency is disguised by the polymerization of the salt to Mo_3Cl_6. Molybdenum is probably *tervalent* in Mo_2O_3, $Mo(OH)_3$, $MoCl_3$, etc. G. Carobbi discussed the isomorphism of tervalent iron and molybdenum salts. According to A. Rosenheim, the complex thiocyanate, $Mo(SCy)_3.3KSCy.4H_2O$, is analogous to the corresponding chromium salt. It is probable that the element is *quadrivalent* in the dioxide, MoO_2; the tetrachloride, $MoCl_4$; the complex oxalates of H. M. Spittle and W. Wardlaw; and the $MoCl_4.6PyHCl$ of J. Sand and A. K. H. Burger. When $MoCy_4.4KCy.2H_2O$ is titrated with potassium permanganate, A. Rosenheim said that it consumes as much oxygen as if the salt were quinquevalent. The element is *quinquevalent* in $MoCl_5$, in the complex salt $MoOCl_3.2RbCl$, and in the oxide Mo_2O_5 of P. Klason, and I. Nordenskjöld. In the molybdenum hexafluoride of O. Ruff and F. Eisner, the element is probably *sexivalent*, and this is possibly also the case with the compounds $MoOF_4$ and MoO_2F_2, as well as with the trioxide, MoO_3, and the molybdates. W. Muthmann and W. Nagel also consider that the element is sexivalent in the permolybdates, but, possibly, it is septivalent in these compounds—*vide infra*. L. Pauling discussed the co-ordination number.

Molybdenum compounds were analyzed by M. H. Klaproth,[2] and C. F. Bucholz, and from these results, J. J. Berzelius inferred that the sulphide has the mol. ratio Mo : S=1 : 2, and molybdic anhydride Mo : O=1 : 3, using the present-day system of at. wts. He also said that chromic and molybdic anhydrides have a similar composition. This conclusion makes the at. wt. of molybdenum approximate to 96. This is in agreement with H. Debray's observation on the density of molybdenum pentachloride, and of A. Vandenberghe on the vap. density of molybdenum trioxide. It is also in agreement with W. Muthmann and W. Nagel's observations on the mol. wt. of Mo_3Cl_6 from its effect on the b.p. of alcohol; and with A. Vandenberghe's observation on the mol. wt. of the pentachloride from its effect on the b.p. of carbon tetrachloride, and with the mol. wt. of $MoO(OH)_2Cl_2$ from its effect on the b.p. of alcohol, acetone, and ether. The at. wt. 96 also fits in with the sp. ht. rule at ordinary temp.—*vide supra;* it also fits in with the isomorphism observed by J. G. Gentele, and R. Funk with the sulphates, chromates, selenates, and molybdates, and the isomorphism observed by F. Ullik with the ammonium magnesium complex salts; with the chemical equivalent observed by E. F. Smith in the precipitation of silver or gold salts by molybdenum; and with the electrochemical equivalent observed by L. Marino, and H. Kuessner. The position assigned to molybdenum in the periodic table of at. wts. is also in harmony with the at. wt. 96; and the same remark applies to the at. number obtained by H. G. J. Moseley, and J. Malmer from the frequency of the X-ray spectral rays.

For the at. wt. of molybdenum, J. J. Berzelius calculated 95 from the ratio $Pb(NO_3)_2 : PbMoO_4$. In 1837, H. Rose made an unsatisfactory attempt to calculate the at. wt. from the ratio Mo : 5Cl; M. Delafontaine also obtained some unsatisfactory results in 1865. L. von Meyer calculated 96·2 from L. P. Liechti and B. Kempe's analyses of the molybdenum chlorides. In 1848, L. F. Svanberg and H. Struve calculated 92 from the ratio $MoO_3 : CO_2$; and 93 to 95 from the ratio $MoS_2 : MoO_3$. N. J. Berlin obtained 96·5 from the ratio $3(NH_4)_2MoO_4.4H_2MoO_4 : MoO_3$; O. F. von der Pfordten, 96·1 from the ratio $3(NH_4)_2MoO_4.4H_2MoO_4 : Mo$; E. F. Smith and P. Maas, 96·03 from the ratio $Na_2MoO_4 : 2NaCl$; and K. Seubert and W. Pollard, 95·92 from the ratio $2AgCl : MoO_3$. J. B. A. Dumas calculated from the ratio $Mo : MoO_3$, 95·9; H. Debray, 95·4; C. F. Rammelsberg, 96·2; K. Seubert and W. Pollard, 95·97; A. Vandenberghe, 96·06; and J. H. Müller, 96·02 to 96·05. F. W. Clarke computed 96·029 for the best representative value for date up to 1910; and J. Meyer, 96·04 up to 1919. The International Table for 1926 gave 96 for the best representative value.

The **atomic number** is 42. F. W. Aston[3] found that molybdenum has seven **isotopes** with mass numbers, and approximate proportions respectively 92 and 14·2; 94 and 10·0; 95 and 15·5; 96 and 17·8; 97 and 9·6; 98 and 23·0; and 100 and 9·8. The packing fractions of Mo^{98} and Mo^{100} are both approximately —5·5 giving an at. wt. of 95·97. M. Gerber considers that his neomolybdenum—*vide supra*—is an isotopic form. N. Bohr's view of the **electronic structure** is symbolized (2) for the K-shell; (4, 4) for the L-shell; (6, 6, 6) for the M-shell; (4, 4, 4) for the N-shell; and (2) for the O-shell. The subject was studied by O. Feussner, R. Ladenburg, H. Lessheim and R. Samuel, C. D. Niven, J. N. Frers, J. D. M. Smith, and E. C. Stoner. According to E. Rutherford and J. Chadwick, and H. Pettersson and G. Kirsch, the **atomic disruption** of molybdenum by α-particles has not yet been proved. The subject was discussed by G. I. Podrowsky.

References.

[1] H. Kauffmann, *Die Valenzlehre*, Stuttgart, 254, 1911; G. Carobbi, *Gazz. Chim. Ital.*, **58**. 35, 1928; W. Muthmann and W. Nagel, *Ber.*, **31**. 3009, 1898; J. Sand and A. K. H. Burger, *ib.*, **38**. 3384, 1905; **40**. 4504, 1907; P. Klason, *ib.*, **34**. 148, 1901; I. Nordenskjöld, *ib.*, **34**. 1573, 1901; O. Ruff and F. Eisner, *ib.*, **40**. 2926, 1907; A. Rosenheim, *ib.*, **42**. 2295, 1909; *Zeit. anorg. Chem.*, **66**. 95, 1910; H. M. Spittle and W. Wardlaw, *Journ. Chem. Soc.*, 792, 1929; R. C. James and W. Wardlaw, *ib.*, 2726, 1928; L. Pauling, *Journ. Amer. Chem. Soc.*, **51**. 1010, 1929.

[2] M. H. Klaproth, *Beiträge zur chemischen Kenntniss der Mineralkörper*, Berlin, **2**. 274, 1797; C. F. Bucholz, *Scherer's Journ.*, **9**. 485, 1802; *Gehlen's Journ.*, **4**. 598, 1805; *Phil. Mag.*, **16**. 193, 1803; J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1818; **23**. 186, 1818; *Lehrbuch der Chemie*, Dresden, **2**. 353, 1844; **3**. 1208, 1845; *Pogg. Ann.*, **8**. 23, 1826; H. Rose, *ib.*, **40**. 400, 1837; L. F. Svanberg and H. Struve, *Svenska Akad. Handl.*, **1**. 9, 1848; *Journ. prakt. Chem.*, (1), **44**. 257, 1848; *Phil. Mag.*, (3), **33**. 409, 524, 1848; N. J. Berlin, *Journ. prakt. Chem.*, (1), **49**. 444, 1850; J. G. Gentele, *ib.*, (1), **81**. 411, 1860; M. Delafontaine, *ib.*, (1), **95**. 138, 1865; *Arch. Sciences Genève*, (2), **23**. 5, 1865; J. B. A. Dumas, *Ann. Chim. Phys.*, (3), **55**. 129, 142, 1859; *Compt. Rend.*, **45**. 709, 1857; H. Debray, *ib.*, **66**. 732, 1868; M. Delauney, *ib.*, **109**. 526, 1889; J. H. Müller, *Journ. Amer. Chem. Soc.*, **37**. 2046, 1915; F. W. Clarke, *ib.*, **22**. 70, 1900; *Amer. Chem. Journ.*, **3**. 263, 1881; *Phil. Mag.*, (5), **12**. 101, 1881; *A Recalculation of the Atomic Weights*, Washington, 354, 1910; J. Meyer in R. Abegg's *Handbuch der anorganischen Chemie*, Leipzig, **4**. i, (2), 477, 1921; F. Ullik, *Sitzber. Akad. Wien*, **55**. 767, 1867; **60**. 295, 1869; L. von Meyer, *Liebig's Ann.*, **169**. 360, 1873; L. P. Liechti and B. Kempe, *ib.*, **169**. 344, 1873; C. F. Rammelsberg, *Sitzber. Akad. Berlin*, 574, 1877; *Ber.*, **10**. 1776, 1877; W. Muthmann and W. Nagel, *ib.*, **31**. 2012, 1898; R. Funk, *ib.*, **33**. 3696, 1900; O. F. von der Pfordten, *Beiträge zur Kenntniss des Molybdäns und Wolframs*, Giessen, 1883; *Zeit. anal. Chem.*, **23**. 413, 611, 1884; A. Vandenberghe, *Mém. Cour. Acad. Belg.*, (4), **56**. 5, 1898; *Zeit. anorg. Chem.*, **10**. 47, 1895; **11**. 385, 397, 1896; K. Seubert and W. Pollard, *ib.*, **8**. 434, 1895; E. F. Smith and P. Maas, *Journ. Amer. Chem. Soc.*, **15**. 397, 1893; *Zeit. anorg. Chem.*, **5**. 280, 1894; E. F. Smith, *ib.*, **1**. 360, 1892; L. Marino, *Gazz. Chim. Ital.*, **35**. ii, 193, 1905; H. Kuessner, *Ueber das anodische Verhalten des Molybdäns, Mangans, Chroms und Tantals*, Halle a. S., 1910; *Zeit. Elektrochem.*, **16**. 754, 1910; H. G. J. Moseley, *Phil. Mag.*, (6), **27**. 703, 1914; J. Malmer, *ib.*, (6), **28**. 787, 1914.

[3] F. W. Aston, *Nature*, **126**. 348, 1930; *Proc. Roy. Soc.*, **130**. A, 302, 1931; *Phil. Mag.*, (6), **49**. 1191, 1925; C. D. Niven, *ib.*, (7), **3**. 1314, 1927; E. C. Stoner, *ib.*, (6), **48**. 719, 1924; N. Bohr, *Nature*, **112**. Suppl., 1923; H. Pettersson and G. Kirsch, *Sitzber. Akad. Wien*, **134**. 491, 1925; *Atomzertrümmerung*, Leipzig, 1926; E. Rutherford and J. Chadwick, *Proc. Phys. Soc.*, **36**. 417, 1924; *Nature*, **113**. 457, 1924; M. Gerber, *Monit. Scient.*, (5), **7**. 73, 121, 169, 219, 1917; O. Feussner, *Zeit. Physik*, **25**. 215, 1924; H. Lessheim and R. Samuel, *ib.*, **42**. 614, 1927; R. Ladenburg, *Naturwiss.*, **8**. 5, 1920; G. I. Podrowsky, *Zeit. Physik*, **57**. 560, 1929; **63**. 561, 1930; J. N. Frers, *Zeit. anorg. Chem.*, **186**. 145, 1930; J. D. M. Smith, *Journ. Chem. Soc.*, 2029, 1927.

§ 7. Alloys and Intermetallic Compounds of Molybdenum

Alloys of molybdenum with some of the metals have been prepared by the fusion of the mixed metals, by reducing the mixed oxides in the electric furnace (C. L. Sargent[1]), or by the alumino-thermite process (A. Stavenhagen and E. Schuchard).

L. Rolla and G. Piccardi studied the ionization produced by mixtures of molybdenum and **sodium.** L. P. Hamilton and E. F. Smith reported that a molybdenum and **copper** alloy can be formed by heating a mixture of the two metals in an electric furnace at 1600°, but their product contained 78·53 per cent. Cu; 8·53, Mo; 2·71, Fe; 2·42, C; and 8·02, gangue. W. Lederer also prepared cupromolybdenum as indicated above, but C. L. Sargent could not get copper to alloy directly with molybdenum. According to L. F. Dreibholz, if purified metals are employed no alloy is formed. The elements are immiscible. He considers that the thermal diagram of the two elements has the form shown in Fig. 8. L. Jordan and co-workers observed that **silver** does not alloy with molybdenum; but, added L. F. Dreibholz, at 1600°, it may dissolve about 5 per cent. of molybdenum—this is rejected during solidification. There is no evidence of molybdenum dissolving silver at 1600°; at this temp., globules of molybdenum float in the silver. Similarly with **gold,** L. F. Dreiholz observed that a little molybdenum may be dissolved at 1500°, but on solidification the molybdenum is rejected. No alloys with the **alkaline earths,** or with **beryllium** have been prepared. N. J. Tram found

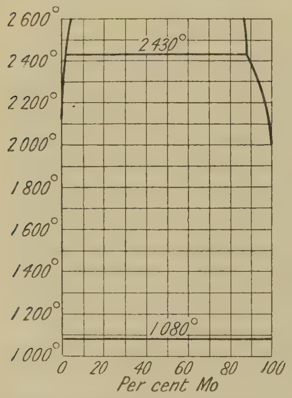


FIG. 8.—Freezing-point Curves of the System: Mo–Cu.

that **magnesium** reacts explosively when heated with molybdenum trioxide, and he added that the product develops hydrogen when treated with water. Alloys of molybdenum and **zinc,** or with **cadmium,** have not been formed. G. Tammann and J. Hinnüber found the solubility of molybdenum in mercury to be too small for measurement. A. S. Russell and co-workers found that between 10^{-5} to 5×10^{-5} grm. per gram of mercury passes into soln. at room temp. G. Tammann and J. Hinnüber, A. Chilesotti, and R. E. Myers obtained **molybdenum amalgams** by the electrolysis of acidic soln. of molybdic acid with a mercury cathode. According to J. Férée, hydrochloric acid of sp. gr. 1·18, sat. with molybdic acid, is diluted with nine times its vol. of water, and electrolyzed with a mercury cathode and a platinum anode, the current being about 5 ampères for each sq. cm. of mercury surface. After some time, the mercury is dried and filtered through chamois leather, when it yields a solid amalgam, **molybdenum enneamercuride,** $MoHg_9$, which is but slightly affected by moist air. When it is subjected to a press. of 200 grms. per sq. cm., it yields another amalgam, **molybdenum dimercuride,** $MoHg_2$, and if this is broken up and again compressed, it yields a third compound, **molybdenum hemitrimercuride,** Mo_2Hg_3, which alters rapidly in moist air. The decomposition of the amalgams under press. is the inverse of the phenomenon observed by W. Spring—**1.** 13, 17. A. S. Russell found that the order of the removal of metals from amalgams by oxidizing agents is Zn, Cu, Cr, Fe, Mo, Co, Hg, Ni, and W.

Alloys of molybdenum and **aluminium** were prepared by F. Wöhler and F. R. Michel, H. Moissan, H. Reimann, and H. Schirmeister. H. Reimann worked with molybdenum disulphide in place of the trioxide. C. Combes was not very successful in preparing alloys by the action of aluminium on molybdenum chloride and sulphides. According to L. Guillet, alloys are obtained by the aluminothermite process, and from the elements. Mixtures of 5 gram-atoms of molybdenum, as MoO_3, and one gram-atom of aluminium furnish **molybdenum icositaluminide,** $AlMo_{20}$, in well-formed crystals which develop no gas with hydrochloric acid; **molybdenum tetritaluminide,** Mo_4Al, from 2 gram-atoms of molybdenum and one gram-atom of aluminium, the crystals are not attacked by hydrochloric acid. With the atomic proportions Mo : Al =1 : 3 fibrous crystals of **molybdenum aluminide,** AlMo, are formed; whilst 1 : 1-mixtures furnish crystals of **molybdenum dialuminide,** Al_2Mo. L. Guillet obtained **molybdenum tetraluminide,** Al_4Mo, in lamellar crystals from the 1 : 1 mixture; and F. Wöhler and F. R. Michel, from a mixture of dry molybdenum fluoride, cryolite, potassium sodium chloride, and aluminium in the proportions 1 : 2 : 2 : 1. The microscopic prisms are black, or iron-grey. They are soluble in hot hydrochloric or nitric acid. L. Guillet prepared crystal aggregates of **molybdenum heptaluminide,** Al_7Mo, by reducing molybdenum trioxide with a large excess of aluminium. There is here nothing to show that any of these products is a chemical individual. H. Reimann said that it is highly probable that **molybdenum tritaluminide,** Al_3Mo, exists as a chemical compound; and he gave Fig. 9 as a probable equilibrium diagram for mixtures with up to 50 per cent. of molybdenum.

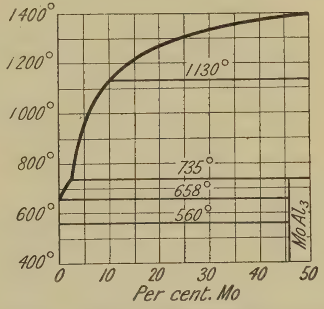


Fig. 9.—Supposed Freezing-point Curve of Mo–Al Alloys.

Alloys of molybdenum with **thallium** or with **tin** have not been reported. L. Rolla and C. Piccardi studied the ionization produced by mixtures of thallium and molybdenum. P. J. Hjelm said that **lead** alloyed with a little molybdenum is whiter and harder than ordinary lead, whilst with more molybdenum, the alloy becomes black and brittle. A. Stavenhagen and E. Schuchard obtained an alloy by the alumino-thermite process; but L. Ott did not obtain it by the electrolysis of a molten mixture of sodium carbonate and molybdate by means of a molten lead cathode.

J. J. Boericke prepared alloys of molybdenum and **vanadium** made by reducing a mixture of a molybdenum or vanadium compound with aluminium in the presence of the alloying metal and a large quantity of an indifferent flux. W. von Bolton obtained alloys with **tantalum.** W. Lederer, C. L. Sargent, and E. Haynes found that alloys of **chromium** and molybdenum can be readily prepared. The alloys were discussed by W. Guertler. E. Siedschlag found that molybdenum dissolves readily in molten chromium until the mass contains 25 per cent. of the former ; in investigating alloys richer in molybdenum, the finely-powdered metals were mixed and compressed into briquettes, which were then heated, but for proportions of molybdenum above 50 per cent., the initial solidification temp. could not be measured. The curve, Fig. 10, shows a eutectic at 1460°, 22·7 per cent. Mo. The liquid is homogeneous, but no mixed crystals are formed below 22·7 per cent. Mo, the solid consisting of chromium crystals and the eutectic mixture ; above this proportion, the solid consists of Mo crystals containing 2·5 per cent. Cr, and the eutectic. The alloys are not likely to be mechanically useful ; those rich in Cr cut glass with remarkable ease. The system copper-molybdenum is heterogeneous in both the liquid and solid states, whilst chromium and copper form no mixed crystals, and are only partly miscible in the liquid state. In the ternary system, Cu–Cr–Mo, the three metals remain separate in the solid state. When electrolytic copper is melted with powdered chromium and molybdenum, no mixed crystals can be detected ; the solids consist of the three metals with the Cr–Cu, and the Cr–Mo eutectics. Alloys of copper with up to ·38 per cent. of Cr should dissolve up to 8 per cent. of Mo, whilst chromium-molybdenum mixtures should dissolve up to 7 per cent. of copper.

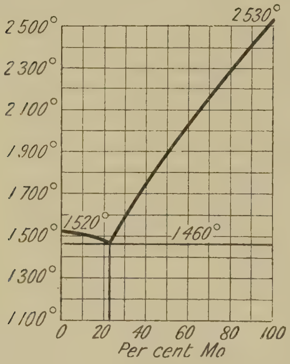


Fig. 10.—Freezing-point Curve of the Mo–Cr Alloys.

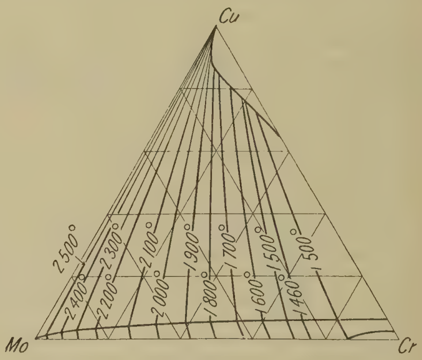


Fig. 11.—Fusion Curves on the Ternary System : Cr–Mo–Cu.

References.

[1] L. Rolla and G. Piccardi, *Atti Accad. Lincei*, (6), **2**. 334, 1925 ; C. L. Sargent, *Journ. Amer. Chem. Soc.*, **22**. 783, 1900 ; A. Stavenhagen and E. Schuchard, *Ber.*, **35**. 909, 1902 ; W. Lederer, *Darstellung und Untersuchung reinen, geschmolzen Molybdäns*, Erlangen, 14, 1911 ; L. F. Dreibholz, *Zeit. phys. Chem.*, **108**. 1, 1924 ; N. J. Tram, *Chem. Ztg.*, **13**. 680, 1889 ; J. Tammann and J. Hinnüber, *Zeit. anorg. Chem.*, **160**. 249, 1927 ; E. Siedschlag, *ib.*, **131**. 191, 1923 ; A. S. Russell and S. W. Rowell, *Journ. Chem. Soc.*, 1881, 1926 ; A. S. Russell, *ib.*, 2398, 1929 ; A. Chilesotti, *Zeit. Elektrochem.*, **12**. 146, 154, 1906 ; L. Jordan, L. H. Grenell and H. K. Herschman, *Trans. Amer. Inst. Min. Eng.*, **75**. 151, 1927 ; R. E. Myers, *Journ. Amer. Chem. Soc.*, **26**. 1124, 1904 ; J. Férée, *Compt. Rend.*, **122**. 733, 1896 ; L. Guillet, *ib.*, **132**. 1322, 1901 ; **133**. 291, 1901 ; *Le Génie Civil*, **41**. 139, 156, 169, 188, 1902 ; H. Moissan, *Bull. Soc. Chim.*, (3), **13**. 966, 1895 ; (3), **15**. 1282, 1896 ; *Ann. Chim. Phys.*, (7), **9**, 337, 1896 ; *Bull. Soc. Enc. Nat. Ind.*, **101**. ii, 232, 1902 ; *Compt. Rend.*, **120**. 1230, 1895 ; C. Combes, *ib.*, **122**. 1482, 1896 ; H. Reimann, *Zeit. Metallkunde*, **14**. 119, 195, 1922 ; W. Guertler, *ib.*, **15**. 151, 251, 1923 ;

H. Schirmeister, *Stahl Eisen*, **35**. 649, 873, 996, 1915; *Beiträge zur Kenntnis der binären Aluminiumlegierungen hintsichtlich ihrer technischen Eigenschaften*, Dusseldorf, 1914; P. J. Hjelm, *Svenska Akad. Nya Hand.*, **9**. 288, 1788; L. Ott, *Elektrolyse geschmolzener Molybdate und Vanadate*, München, 23, 1911; E. Haynes, *Trans. Amer. Inst. Min. Eng.*, **44**. 573, 1913; **54**. 3, 1915; L. P. Hamilton and E. F. Smith, *Journ. Amer. Chem. Soc.*, **23**. 151, 1901; J. J. Boericke, *U.S. Pat. No.* 1562201, 1925; W. von Bolton, *Zeit. Elektrochem.*, **11**. 47, 1905; F. Wöhler and F. R. Michel, *Liebig's Ann.*, **115**. 102, 1860.

§ 8. Molybdenum and Molybdic Oxides

According to J. J. Berzelius,[1] **molybdenum monoxide,** or **molybdous oxide,** MoO, is formed as a purple or violet powder when zinc and hydrochloric acid are allowed to act for a long time on fused or sublimed molybdenum trioxide; but the product is probably molybdic oxide. W. Muthmann and W. Nagel could not prepare this oxide. C. W. Blomstrand thought that **molybdous hydroxide,** $Mo(OH)_2$, is formed as a black solid by the action of conc. potash-lye on molybdenum dibromide, but he later represented it as $Mo_3(OH)_6$. W. Muthmann and W. Nagel found that the hydrogen is given off while the black precipitate is being formed, and they find that it is molybdic hydroxide, $Mo(OH)_3$. The same product is obtained by the action of potash-lye on molybdenum dihydroxytetrabromide, $Mo_3(OH)_2Br_4+4KOH+3H_2O=3Mo(OH)_3+4KBr+3H$. This makes it doubtful if a bivalent molybdenum compound has yet been prepared.

What J. J. Berzelius [2] called molybdous oxide was shown by C. W. Blomstrand, and C. F. Rammelsberg to be hydrated **molybdic oxide,** or **molybdenum sesquioxide,** or **molybdenum hemitrioxide,** Mo_2O_3. J. J. Berzelius obtained the hydrated oxide by the action of reducing agents on a soln. of a molybdenum salt or of molybdic acid. Thus, by treating a hydrochloric acid soln. of molybdenum chloride, standing over mercury, with liquid potassium amalgam, added drop by drop, the soln. becomes greenish, and then black and opaque. As soon as the oxide begins to separate, the soln. is decanted, and the hydroxide is precipitated by ammonia, washed, dried over sulphuric acid in vacuo, and heated out of contact with air. If an excess of hydrochloric acid be not present, a higher dark brown oxide is precipitated instead of the black molybdic oxide. As indicated above, this oxide was also obtained by the prolonged action of hydrochloric acid and zinc on fused or sublimed molybdenum trioxide; and also by the action of zinc on a conc. soln. of ammonium or alkali molybdate in an excess of hydrochloric acid so that the molybdic acid first precipitated is redissolved. The soln. becomes blue, then reddish-brown, and finally black. It is then poured off the zinc and mixed with enough aq. ammonia to precipitate the molybdic oxide alone. The precipitate is washed with dil. aq. ammonia to remove the zinc oxide, and afterwards with cold water. It is then pressed, dried over sulphuric acid in vacuo, and heated out of contact with air. M. Guichard found that the hydrated form alone exists because, when the black product $Mo(OH)_3$ is dehydrated, internal oxidation occurs, and the composition is not Mo_2O_3. Modifications of this process were used by J. Sopp, A. Atterberg, C. F. Rammelsberg, A. C. Chapman and H. D. Law, D. L. Randall, M. Guichard, A. Chilesotti, A. Wernecke, F. Pisani, and I. Macagno. C. W. Blomstrand used magnesium, zinc, or zinc coated with cadmium, and sulphuric or hydrochloric acid, washing out the zinc salts by very dilute hydrochloric acid. F. von Kobell boiled lead molybdate with hydrochloric acid and copper; C. F. Rammelsberg, and H. Hirzel used ammonium molybdate or molybdic acid. C. Paal and H. Büttner found that the reduction of ammonium molybdate by colloidal palladium at ordinary temp. yields hydrated molybdenum dioxide, but at 50° to 60°, under a slight press., hydrated molybdic oxide is formed. If the reduction occurs in the presence of a protective colloid—sodium protalbinate—**colloidal molybdenum trihydroxide** is formed. L. F. Svanberg and H. Struve obtained this oxide by heating molybdenum trioxide in dry hydrogen—*vide supra*, the preparation of molybdenum—and E. F. Smith and W. S. Hoskinson, E. T. Wherry and E. F. Smith, and E. F. Smith obtained *molybdic hydroxide*, $Mo_2O_3.3H_2O$, or $Mo(OH)_3$, by the electrolysis of a neutral soln. of ammonium molybdate, or a soln. acidified with sulphuric acid. J. J. Berzelius, and C. W. Blomstrand also obtained the hydrated oxide by adding potash-lye to a soln. of molybdenum dichloride or dibromide, and W. Muthmann and W. Nagel found that hydrogen is simultaneously evolved.

Molybdic oxide is pitch-black, and is slowly oxidized by exposure to air. In some cases J. J. Berzelius observed that when heated in vacuo, it may show a feeble calorescence—*vide* **5**. 33, 10. P. Sabatier and J. B. Senderens found that when heated to about 500° in nitrous oxide, it yields a mixture of molybdenum dioxide, and trioxide; and in nitric oxide, molybdenum dioxide. J. J. Berzelius observed that it is insoluble in soln. of potassium hydroxide, ammonia, or ammonium carbonate. Acids do not dissolve the anhydrous oxide; and the hydroxide is dissolved with difficulty to form molybdic salts. F. Isambert said that soln. of the oxide in acids are black. The salts of tervalent molybdenum were studied by F. A. Gooch and O. S. Pulman, F. Pisani, C. F. Rammelsberg, and W. Wardlaw and W. H. Parker. G. Unger, G. Reissaus, and E. Müller studied the electrometric oxidation of soln. of tervalent molybdenum with permanganate. R. Montequi, and J. Koppel prepared compounds with the xanthates—*e.g.* $(C_2H_5OCS_2)_4Mo_2O_3$.

References.

[1] J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817; *Pogg. Ann.*, **4**. 153, 1825; **6**. 331, 369, 1826; **7**. 261, 1826; *Ann. Chim. Phys.*, (2), **17**. 5, 1821; W. Muthmann and W. Nagel, *Ber.*, **31**. 2009, 1898; C. W. Blomstrand, *Oefvers. Akad. Förh.*, **14**. 393, 1857; *Journ. prakt. Chem.*, (1), **77**. 91, 1859.

[2] J. Sopp, *De acidi phosphorici et molybdaenici nova metandi ratione*, Bonnae, 7, 1857; A. Atterberg, *Några bidrag till kännedon om molybden*, Stockholm, 72, 1872; C. W. Blomstrand, *Chlorens förhallande till molybden*, Lund, 1855; *Journ. prakt. Chem.*, (1), **71**. 455, 1857; (1), **72**. 408, 1861; (1), **77**. 91, 1859; *Skand. Nat. Förh.*, **8**. 509, 1860; *Oefvers. Akad. Förh.*, **14**. 393, 1857; C. F. Rammelsberg, *Pogg. Ann.*, **127**. 285, 1865; *Zeit. anal. Chem.*, **5**. 203, 1866; *Journ. prakt. Chem.*, (1), **97**. 174, 1866; J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817; *Pogg. Ann.*, **4**. 153, 1825; **6**. 331, 369, 1826; **7**. 261, 1826; *Ann. Chim. Phys.*, (2), **17**. 5, 1821; E. F. Smith and W. S. Hoskinson, *Amer. Chem. Journ.*, **7**. 90, 1885; *Chem. News*, **53**. 278, 1885; E. F. Smith, *Ber.*, **13**. 751, 1880; *Amer. Chem. Journ.*, **1**. 329, 1880; E. T. Wherry and E. F. Smith, *Journ. Amer. Chem. Soc.*, **29**. 806, 1907; F. Streintz, *Ann. Physik*, (4), **9**. 854, 1902; M. Guichard, *Ann. Chim. Phys.*, (7), **23**. 504, 1901; P. Sabatier and J. B. Senderens, *ib.*, (7), **7**. 348, 1896; *Bull. Soc. Chim.*, (3), **13**. 870, 1885; *Compt. Rend.*, **114**. 1429, 1892; **120**. 618, 1895; F. Pisani, *ib.*, **59**. 301, 1864; F. Isambert, *ib.*, **80**. 1087, 1875; I. Macagno, *Gazz. Chim. Ital.*, **4**. 567, 1874; A. Werncke, *Zeit. anal. Chem.*, **14**. 1, 1875; F. von Kobell, *Anz. Gelehrte München*, 907, 1847; *Journ. prakt. Chem.*, (1), **41**. 158, 1847; H. Hirzel, *Zeit. Pharm.*, **2**. 2, 1850; L. F. Svanberg and H. Struve, *Svenska Akad. Handl.*, **1**. 9, 1848; *Journ. prakt. Chem.*, (1), **44**. 257, 1848; *Phil. Mag.*, (3), **33**. 409, 524, 1848; W. Wardlaw and W. H. Parker, *Journ. Chem. Soc.*, **127**. 1311, 1487, 1925; A. C. Chapman and H. D. Law, *Analyst*, **32**. 250, 1907; D. L. Randall, *Amer. Journ. Science*, (4), **24**. 313, 1907; F. A. Gooch and O. S. Pulman, *ib.*, (4), **12**. 449, 1901; *Zeit. anorg. Chem.*, **29**. 353, 1902; C. Paal and H. Büttner, *Ber.*, **48**. 220, 1915; W. Muthmann and W. Nagel, *ib.*, **31**. 1836, 2009, 1898; A. Chilesotti, *Zeit. Elektrochem.*, **12**. 146, 197, 1906; E. Müller, *ib.*, **33**. 182, 1927; E. Müller and H. Möllering, *Zeit. anorg. Chem.*, **141**. 111, 1924; G. Unger, *Manganalytische Bestimmung von reduzierten Molybdänlösungen unter Zuhilfenahme der Potentiometrie*, Dresden, 1926; E. Fricke, *Ueber die elektrolytische Reduktion von Molybdänlösungen una die aus reduzierten wässerigen Lösungen zu gewinnenden Salze des Molybdäns niederer Wertigkeitsstufen*, Dresden, 1923; G. Reissaus, *Metall Erz*, **21**. 118, 1924; J. Koppel, *Chem. Ztg.*, **43**. 777, 1919; R. Montequi, *Anal. Fis. Quim.*, **4**. 542, 1916; **28**. 479, 1930.

§ 9. Intermediate Oxides—MoO_2 to MoO_3

C. F. Bucholz[1] prepared **molybdenum dioxide**, MoO_2, by gently heating the metal for a short time in air; and J. J. Berzelius found that the lower oxide, free from zinc oxide, burns with a feeble glow when it is heated in air. L. F. Svanberg and H. Struve obtained this oxide by heating molybdenum trioxide; and H. Rose, and L. F. Svanberg and H. Struve, by heating ammonium molybdates. C. F. Rammelsberg said that the product is not homogeneous. C. F. Bucholz also heated ammonium molybdate in a covered crucible, and J. J. Berzelius added that the dioxide so produced is contaminated with molybdenum trioxide which can be removed by potash-lye, or by hydrofluoric acid. According to E. Uhrlaub, this product, as well as that obtained by J. J. Berzelius—by igniting in a covered crucible a mixture of sodium molybdate and ammonium chloride, and washing the products with water—contains nitrides (*q.v.*). The dioxide was also obtained by L. F. Svanberg and H. Struve, D. K. Tuttle, N. J. Berlin, W. Muthmann, and M. Guichard by heating a mixture of ammonium molybdate and molybdenum trioxide, or a mixture of sodium molybdate and ammonium chloride, and washing the residue with aq. ammonia, and then with hydrochloric acid. F. Mauro and R. R. Panebianco obtained crystals of the dioxide by heating a mixture of 14·4 grms. MoO_3, 14 grms. K_2CO_3, and 7 grms. B_2O_3 for 3 or 4 hrs. at a high temp., and washing the cold mass successively with aq. ammonia, water, hydrochloric acid, and water. W. Muthmann obtained the dioxide by fusing a mixture of anhydrous ammonium molybdate, molybdenum trioxide, potassium carbonate, and boric acid in the proportions 8 : 7 : 14 : 7 by weight. H. Debray obtained an oxide, possibly the dioxide, by heating molybdenum trioxide in a mixture of steam and hydrogen. L. P. Liechti and B. Kempe reduced the trioxide to dioxide by heating it in a current of hydrogen. M. Guichard studied the equilibrium conditions in the balanced reaction: $Mo+2H_2O \rightleftharpoons MoO_2+2H_2$—*vide supra.* C. Friedheim and M. K. Hoffmann also reduced molybdenum trioxide with hydrogen at 450°, and removed the unchanged trioxide as volatile oxychloride by heating the product in a current of hydrogen chloride. H. Debray also used a mixture of carbon monoxide and dioxide as the reducing agent. L. F. Svanberg and H. Struve obtained the dioxide by heating to redness for several hours an alkali molybdate in hydrogen and washing the product; F. Ullik heated a mixture of sodium trimolybdate and zinc, and washed product with a soln. of potassium hydroxide and then with hydrochloric acid. C. Paal and H. Büttner reduced ammonium molybdate with colloidal palladium at ordinary temp. and obtained molybdenum dioxide. W. Püttbach obtained the dioxide by heating molybdenum dioxydichloride in carbon dioxide or in hydrogen; and E. Friederich and L. Sittig by heating to about 1200° a mixture of 4·8 grms. of molybdenum powder and 14·4 grms. of molybdenum trioxide. H. Buff, and M. Guichard obtained the dioxide by the electrolysis of fused molybdenum trioxide, or potassium molybdate; and L. Ott, by the electrolysis of molten sodium or barium molybdate using a high current density.

Analyses in agreement with the formula MoO_2 were made by J. J. Berzelius, C. F. Bucholz, F. Ullik, and M. Guichard. Molybdenum dioxide is described by L. F. Svanberg and H. Struve as a brownish-black powder; L. Ott, as a violet crystalline powder; and F. Ullik, as forming dark bluish-violet prisms which appear pale violet-red in transmitted light. F. Mauro and R. R. Panebianco said that the bipyramidal crystals are tetragonal with the axial ratio $a : c=1 : 0·5774$; but S. Stevanovic showed that the pseudotetragonal crystals are monoclinic prisms with the axial ratios $a : b : c=0·9869 : 1 : 0·5765$, and $\beta=91° 34'$. V. M. Goldschmidt and co-workers, M. L. Huggins, and L. Pauling discussed the lattice-structure. The X-radiogram shows that the space-lattice is of the rutile-type with $a=4·86$ A., and $c=2·79$ A., so that $a : c=1 : 0·573$. S. Stevanovic gave for the sp. gr. 6·34; and F. Mauro and R. R. Panebianco, 6·44. W. Biltz studied the mol. vol. N. Parravano and G. Malquori gave for the dissociation press., $\log p=-27·843$ at 600°. W. G. Mixter gave 142·8 Cals. for the heat of formation from its elements. B. A. Dima studied the photoelectric effect of the oxide. J. Vrede observed that the dioxide has no value as a radio-detector. F. Ullik, and M. Guichard observed that it is a good electrical conductor; E. Friederich and L. Sittig gave $40·0\times10^{-4}$ ohm for the resistance of a metre wire 1 sq. mm. cross-section at 1000°; and the temp. coeff. is negative; and E. Wedekind and C. Horst found that its magnetic susceptibility is greater than that of the metal, being $0·33\times10^{-6}$ mass unit at 19·5°. S. Berkman and H. Zocher gave $0·09\times10^{-6}$ mass unit.

M. Guichard found that the oxide is reduced by hydrogen to the metal without the formation of intermediate oxides—a subject discussed by G. Martin. The equilibrium conditions were studied by M. Guichard—*vide supra.* G. Chaudron studied the equilibrium conditions in the reaction: $2H_2O+Mo \rightleftharpoons MoO_2+2H_2$ over the temp. range 700° to 1100°. H. Debray found that water vapour at a red-heat oxidizes the dioxide to the trioxide; H. Rose found that chlorine converts the dioxide into the dioxydichloride; and A. Vandenberghe, and C. Friedheim and M. K. Hoffmann, that it does not volatilize when heated in hydrogen chloride. J. J. Berzelius found that the dioxide is not soluble in hydrofluoric, hydrochloric or sulphuric acid. W. R. E. Hodgkinson and F. K. S. Lowndes found that if a little dioxide be added to molten potassium chlorate, oxygen and chlorine are evolved. J. J. Berzelius said that a little dioxide dissolves in boiling, conc. sulphuric acid; and it dissolves slowly in fused alkali hydrosulphate. It is converted by nitric acid into the trioxide. C. Friedheim and M. K. Hoffmann observed that the dioxide is decomposed when heated in carbon dioxide; and A. Michael and A. Murphy, that carbon tetrachloride converts it into molybdenum tetrachloride. W. Skey, and E. Péchard observed that thiocyanates produce a red coloration with the dioxide. J. J. Berzelius found that the dioxide does not dissolve in a boiling soln. of potassium hydrotartrate. G. Rauter found that silicon tetrachloride has no action on the dioxide. J. J. Berzelius found that the dioxide is insoluble in soln. of alkali hydroxide or carbonate. F. Ullik observed that a crystal of molybdenum dioxide in a soln. of copper sulphate, and in contact with zinc, quickly becomes covered with a film of copper. E. F. Smith and O. L. Shinn found that a mol of the dioxide liberates two gram-atoms of silver from an ammoniacal soln. of silver nitrate: $MoO_2+2Ag^{\cdot}\rightarrow MoO_3+2Ag$, etc.; salts of copper and mercury are not so reduced. C. Friedheim and M. K. Hoffmann found that ferric sulphate oxidizes the dioxide to trioxide. The electrometric oxidation of soln. of quadrivalent molybdenum by permanganate was studied by G. Unger, E. Fricke, G. Reissaus, and E. Müller. C. Engler and L. Wöhler discussed molybdenum dioxide as a catalytic agent. M. Guichard was at first inclined to believe that the dioxide does not form salts, although J. J. Berzelius, H. Rose, and others have described a series of salts.

J. J. Berzelius, H. Rose, and C. F. Rammelsberg described what they considered to be hydrated molybdenum dioxide, obtained by adding alkali-lye to soln. of more or less reduced molybdic acid. P. Klason showed that in all probability these products are impure molybdenum pentahydroxide, and that the tetrahydroxide does not exist.

This remark applies to the so-called *monohydrate*, $MoO_2.H_2O$, of E. Péchard, produced by the electrolysis of a hydrochloric or oxalic acid soln. of ammonium molybdate; or by adding alkali-lye to a hydrochloric acid soln. of alkali molybdate mixed with potassium iodide; and to the *dihydrate*, $MoO_2.2H_2O$, reported to be formed by adding ammonia to a hot hydrochloric acid soln. of acid ammonium molybdate and potassium iodide. O. W. Gibbs obtained some complexes with tungstic acid—*e.g.* $5K_2O.12WO_3.MoO_2.16H_2O$. The *trihydrate*, $MoO_2.3H_2O$, was said by F. J. Faktor to be produced by the action of sodium thiosulphate on a soln. of ammonium molybdate; and G. Krüss obtained the *hemiheptadecahydrate*, $2MoO_2.15H_2O$, by the action of conc. alkali-lye on the oxysulphide, $(NH_4)H.Mo_2O_4S_4$.

C. Paal and co-workers, however, found that a soln. of ammonium paramolybdate in the presence of a little colloidal palladium is reduced at room temp. by hydrogen at normal press. to form a greenish-black precipitate approximating the monohydrate, $MoO_2.H_2O$, or $MoO(OH)_2$, when dried at ordinary temp., and it yields the dioxide, MoO_2, if dried at a higher temp. If the reduction occurs in the presence of a protective colloid—sodium protalbinate—**colloidal molybdenum tetrahydroxide** is formed at ordinary temp. H. Freundlich and W. Leonhardt found that the monohydrate obtained by E. Péchard—by precipitation with alkali hydroxide from the soln. produced by the action of potassium iodide on hydrochloric acid soln. of alkali molybdate or by the electrolysis of hydrochloric or oxalic acid soln. of molybdic acid—behaves towards water like a colloid. The coagulated dioxide shows differences in the readiness with which it undergoes peptization, in that the sol form is more readily produced from coagulates which have been precipitated by the less active electrolytes. Low temp. is also favourable to the re-formation of the sol. The coagulation by electrolytes depends on the cation.

According to W. Muthmann, the compound **magnesium hypomolybdate,** $2MgO.3MoO_2$, is formed by fusing sodium trimolybdate with magnesium oxide; and zinc oxide similarly furnishes **zinc hypomolybdate,** $2ZnO.3MoO_2$.

J. J. Berzelius digested in a stoppered flask, at 40°–60°, a mixture of powdered molybdenum and a soln. of molybdic acid ; the soln. became dark blue, and finally green. The addition of ammonium chloride to the green soln. precipitates an olive-green oxide which redissolves in water—presumably as a peptized colloid. A soln. of the brown and blue molybdenum oxides in hydrochloric acid precipitates a green oxide on the addition of ammonia. C. F. Bucholz obtained a pale blue oxide which J. J. Berzelius supposed to be the same as the green oxide. W. Muthmann could not prepare an olive-green oxide of constant composition. J. Reich obtained the blue soln. by the action of lead on a soln. of molybdic acid ; and the green soln. by the electrolysis of a soln. of 2 grms. of molybdenum trioxide in aq. ammonia mixed with sulphuric acid and diluted with water, by means of platinized platinum electrodes and a current density of 0·5 amp. per sq. dm. Many blue oxides have been reported, and the differences in the analysis probably turn on the presence of variable proportions of molybdenum trioxide. M. Guichard added that if the trioxide be removed by successive washing with soda and hydrochloric acid, molybdenum dioxide is the sole oxide formed by the action of heat on a mixture of molybdenum trioxide and ammonium molybdate, or by the electrolysis of fused molybdenum trioxide.

According to W. Muthmann, the blue oxide which is formed by the action of reducing agents on soln. of molybdic acid, or by boiling molybdenyl sulphate with powdered molybdenum, is **molybdenum tritoctoxide,** Mo_3O_8. The olive-green oxide prepared by J. J. Berzelius is probably a mixture of this oxide with the tetrahydroxide, $Mo(OH)_4$. If a soln. of molybdenum in conc. sulphuric acid be heated to a high temp., a mixture of the tritoctoxide and trioxide is formed. A. Rogers and F. H. Mitchell obtained the tritoctoxide by adding stannous chloride to a soln. of ammonium molybdate slightly acidified with nitric acid ; washing the precipitate as quickly as possible; and drying it at 100°. According to L. A. Munro, by the addition of excess of stannous chloride, a green and then brown soln. can be obtained due to further (reversible) reduction. Molybdenum-blue forms a (negative) colloidal soln. which can be bleached by animal charcoal, partly by absorption and partly by oxidation. It can also be obtained in the crystalloidal form by dialyzing the colloidal soln., precipitating the hydrogel with ammonium chloride, and evaporating the remaining soln. E. J. Millard obtained the blue oxide by adding a soln. of ammonium molybdate and a little sulphurous acid to a soln. of hypophosphite ; H. Buff, by the electrolysis of molten molybdenum trioxide with platinum electrodes ; C. F. Rammelsberg, by heating ammonium molybdenum dioxymolybdate in a closed vessel ; C. Bärwald, by melting a mixture of ammonium peroxymolybdate and molybdenum trioxide in a closed vessel ; and N. J. Berlin, by melting a mixture of ammonium 3 : 7-molybdate and molybdenum trioxide in a covered crucible, and washing the product with aq. ammonia—E. Uhrlaub said that the product is contaminated with nitride. Analyses in agreement with Mo_3O_8 were made by W. Muthmann, C. Bärwald, N. J. Berlin, and C. F. Rammelsberg. L. A. Munro found that the formula obtained by analysis of the hydrogel is approximately $Mo_3O_8.H_2O$, but since the substance is readily soluble in alcohol the water is probably not combined as hydrate; hence the true formula is Mo_3O_8. This oxide was said by H. Buff to form copper-red crystal plates ; and by C. Bärwald, a bluish-violet crystalline powder. H. Buff observed that the oxide is a good conductor of electricity, and that in air it acquires a bluish film. A. Rogers and

F. H. Mitchell said that the oxide is more easily reduced by hydrogen than is molybdenum trioxide. W. Muthmann said that the tritoctoxide is not attacked by hydrochloric and sulphuric acids, or by aq. ammonia ; it is easily oxidized by nitric acid ; and it is decomposed by alkali-lye. According to J. Duclaux and R. Titéica, molybdenum blue is an acid comparable in strength with mineral acids, the colloidal anion of which contains molybdenum in two states of oxidation and is capable of union with metallic ions to form salts. Molybdenum-blue is peculiar in its solubility in a large number of organic solvents, whilst it is insoluble in all liquids of low dielectric constant. When certain organic solvents are shaken with an aq. soln. of molybdenum-blue, the aq. soln. is almost immediately decolorized, the molybdenum compound passing into the organic liquid phase. This is the first example recorded of a colloid passing from one solvent into another ; glycerol appears to be the best solvent. The solubility in butyl alcohol provides a rapid means of purifying molybdenum-blue by extraction of the aq. soln.

H. Höfer[2] described a complex molybdenum oxide which he found embedded in the barytes and wulfenite at Bleiberg, Carinthia. It appeared to have been formed by the decomposition of the metal molybdates by acidic waters. W. T. Schaller suggested that it is formed by the alteration of molybdenite, jordisite, wulfenite, and molybdosodalite. H. Höfer called the mineral **ilsemannite**—after J. C. Ilsemann. Ilsemannite is bluish-black or black, and cryptocrystalline. It becomes blue on exposure to air, and it has been called *natural molybdenum blue*. It forms a deep blue soln. with water ; and the aq. soln. yields blue crystals on evaporation. H. Höfer considered it to have the composition of J. J. Berzelius' $MoO_2.4MoO_3$; C. F. Rammelsberg gave the formula Mo_2O_5, or $MoO_2.MoO_3$. W. Muthmann said that its composition is not Mo_5O_{14}, as supposed by H. Höfer, but is nearer to Mo_3O_8. More probably, ilsemannite is a mixture. F. Cornu represented it as **colloidal molybdenum tritoctoxide,** $Mo_3O_8.nH_2O$, and added that it is the only reversible colloid occurring in nature. The subject was discussed by A. Himmelbauer, E. Dittler, F. L. Hess, H. F. Yancey, and C. W. Greenland. W. T. Schaller obtained from Ouray, Utah, a mineral of the composition $MoO_3.SO_3.5H_2O$, which he called ilsemannite, but H. F. Yancey did not agree that this represents the composition of ilsemannite. E. Dittler supposed ilsemannite to be an oxidation product of molybdenite. When molybdenum sulphate soln. are treated with ferrous sulphate, free molybdenum trioxide separates. This when washed contains no iron or sulphate, but is reduced to $Mo_3O_8.H_2O$. Some varieties are free from iron, so that W. T. Schaller's hypothesis is based on samples in which the sulphate was an accidental constituent.

W. Biltz[3] prepared colloidal molybdenum tritoctoxide, and found that the hydrosol passes to the anode on electrolysis. A. Dumansky showed that when molybdenum trioxide suspended in water, is heated on a water-bath with a large excess of powdered metallic molybdenum, a soln. of the oxide Mo_3O_8 is obtained, which, according to cryoscopic measurements, contains unpolymerized mols. of the oxide. On addition of ammonium chloride, barium chloride, and other salts to this soln., polymerization takes place, and the oxide passes into the colloidal form. W. Biltz found that the colloid is adsorbed from its sol by fibres of cotton, wool, and especially silk. C. Winssinger observed that the absorption spectrum is similar to that produced by colloidal molybdenum sulphide.

C. F. Bucholz prepared what appears to have been the colloidal *pentahydrate* of molybdenum tritoctoxide by exposing moist molybdenum, or the hydrated trioxide to air for a long time, or boiling these substances with water in an open vessel. He also made it by boiling in water a mixture of molybdenum with twice its weight of molybdenum trioxide, and evaporating the blue soln. out of contact with air, or in contact with molybdenum. J. J. Berzelius prepared this hydrate by mixing a soln. of molybdenum dioxide in hydrochloric acid with a soln. of ammonium 3 : 7-molybdate, and collecting the precipitated oxide which is washed, first with water containing ammonium chloride, and then with alcohol or cold water.

It is dried in air. O. Maschke dissolved calcium molybdate in warm, dil. hydrochloric acid and added sucrose or glucose, boiled the mixture for a few minutes, added a soln. of sodium or calcium chloride, and washed the precipitate first with the precipitant and then with a little water. G. Marchetti dissolved molybdenum in conc. aqua regia, and after all the nitric acid had been expelled by evaporating the soln. on a water-bath, with the addition of hydrochloric acid, diluted the filtered soln., and reduced it by an electric current. The dark blue liquid yields crystals of the pentahydrate. C. F. Bucholz described his product as a dark indigo-blue powder; and G. Marchetti obtained dark blue, almost black, triclinic crystals. J. J. Berzelius said that all the water can be driven off by heating the crystals in vacuo. C. F. Bucholz said that the salt is fairly soluble in water forming a blue soln. which, according to G. Marchetti, does not give a precipitate on adding ammonium chloride. Cryoscopic determinations show that in aq. soln. the pentahydrate is neither ionized nor polymerized. J. J. Berzelius said that the aq. soln. becomes paler in air owing to oxidation. Alcohol dissolves a little of the hydrated oxide. O. Maschke found that the aq. soln. is easily decolorized by alkalies, chlorine, nitrous acid, hydrogen dioxide, permanganic acid, etc. L. Schönn said that the blue soln. is first decolorized by hydrogen dioxide, and then forms a yellow liquid. According to G. Marchetti, aq. ammonia, and alkali-lye extract molybdenum trioxide and leave the dioxide; whilst very dilute alkali-lye dissolves all the oxide, and when the soln. is boiled, it deposits molybdenum dioxide. Acids do not appear to form salts. C. F. Rammelsberg obtained **ammonium dimolybditetramolybdate,** $(NH_4)_2O.2MoO_2.4MoO_3.9H_2O$, or $(NH_4)_2O.(Mo_3O_8)_2.9H_2O$, as brown crystals under the blue precipitate by allowing a mixed soln. of molybdenum dioxide and ammonium molybdate in hydrochloric acid to stand for some time. The brown crystals form a brown soln. with water, and the addition of silver nitrate to the soln. gives a yellow precipitate soluble in nitric acid. The salt gives off water and ammonia when heated.

According to C. F. Rammelsberg,[4] the precipitate formed on mixing a hydrochloric acid soln. of molybdenum dioxide and molybdic acid, when washed with an alcoholic soln. of ammonium chloride, and dried over sulphuric acid, is the *trihydrate* of **molybdenum hemipentoxide,** $Mo_2O_5.3H_2O$, or $MoO(OH)_3$. J. Reich said that the electro-reduction of a soln. of 2 grms. of molybdenum trioxide in 11 grms. of sulphuric acid, and 100 c.c. of water with a current density of 0·005 amp. per sq. dm., and 0·49 volt gives a blue deposit of the hemipentoxide. P. Klason made it by adding exactly three mols of ammonia to an aq. soln. of a mol of ammonium molybdenyl chloride. The precipitate resembles freshly-precipitated ferric hydroxide, only it is brighter in colour; sodium acetate can also be used as a precipitant. It is soluble in water to the extent of 2 parts in 1000, but insoluble in the presence of ammonium chloride; it has no acid properties, since it does not dissolve in aq. alkali hydroxides, and is only slightly soluble in ammonia and alkali carbonates. If in its preparation an excess of ammonia be used, the hydroxide is partially decomposed, and the filtered soln. contains much molybdic acid, as stated by H. Debray. P. Klason added that molybdenum blue does not contain molybdenum dioxide as assumed by M. Guichard, but rather the hemipentoxide. The anhydrous oxide, Mo_2O_5, was obtained by C. F. Rammelsberg, by dehyrating the hydrate in vacuo; or, in a current of carbon dioxide. E. Péchard obtained it by heating a mixture of ammonium molybdate, potassium iodide, and hydrochloric acid. E. Friederich and L. Sittig obtained the hemipentoxide by heating to about 1200° a mixture of 2·4 grms. of molybdenum powder and 18 grms. of molybdenum trioxide. E. Friederich gave 9·5 ohms for the resistance of a metre wire 1 sq. mm. cross-section. E. F. Smith and V. Oberholtzner treated the trioxide at 105°–120° with dry hydrogen iodide, and obtained a blue *hemitrihydrate*, $Mo_2O_5.1·5H_2O$, which was stable in air, and at a red-heat furnished brown hemipentoxide. W. Wardlaw and F. H. Nicholls obtained molybdenum hemipentoxide, Mo_2O_5, by heating the oxysulphate, $Mo_2O(SO_4)_2 \rightarrow Mo_2O_5 + 2SO_2$, or the oxyoxalate, $Mo_2O(C_2O_4)_2 \rightarrow Mo_2O_5$

+4CO. In opposition to the statement of M. Guichard, the pentoxide is almost unchanged when boiled five successive times in aq. ammonia, washed with distilled water, and dried at 100°. A little molybdenum passes into soln., but there is no evidence that the product is impure dioxide. J. Vrede found the oxide has no value as a radio-detector; and W. Meissner, that it is not a super-conductor. E. Friederich and L. Sittig, found the sp. resistance of the dark violet hemipentoxide to be $9{\cdot}5\times10^{-4}$ ohm at 1000°, and the temp. coeff. is negative. A. Schulze discussed the super-conducting qualities of the oxide. E. Newbery and J. N. Pring found that the pentoxide is reduced to the monoxide by hydrogen at 2000° and 150 atm. press. The violet-black powder, said E. Péchard, is easily soluble in water, and when hydrogen dioxide is added to the dark blue aq. soln., the colour becomes green, and then yellow. P. Klason, and W. Wardlaw and F. H. Nicholls, said that the hemipentoxide dissolves with difficulty in hydrochloric and sulphuric acids, and this the more slowly, the higher the temp. of preparation. G. Reissaus, E. Fricke, G. Unger, and E. Müller studied the electrometric oxidation of soln. of quinquevalent molybdenum with permanganate. S. Ghosh and N. R. Dhar studied the sensitization of the negative colloid, by other colloids. G. A. Barbieri studied the action of molybdenum hemipentoxide on formic and oxalic acids. P. Sabatier and A. Mailhe, and J. N. Pearce and A. M. Alvarado studied the dehydrating action on ethyl alcohol. P. Sabatier and A. Mailhe, and J. N. Pearce and A. M. Alvarado observed that this oxide acts catalytically in decomposing formic acid into carbon dioxide, carbon monoxide, water, and hydrogen; and formaldehyde, into carbon dioxide and water. The hemipentoxide was also prepared by F. Mawroff and M. Nikoloff, who also observed that when the violet molybdenum oxyhypophosphite is rubbed with aqua ammonia, the yellowish-brown precipitate can be washed and dried. It dissolves sparingly in water, and the aq. soln. has a neutral reaction. If dissolved in acids, and precipitated by ammonia, and washed with dil. aq. ammonia and then with absolute alcohol, the residue has the composition of **ammonium molybdenum hemipentoxide,** $NH_4Mo_2O_5.3H_2O$, which, when ignited in a current of carbon dioxide, yields molybdenum pentoxide. If sodium hydroxide soln. be used in place of ammonia, **sodium molybdenum hemipentoxide,** $NaMo_2O_5.3H_2O$, is formed, and this, on ignition, yields the anhydrous form $NaMo_2O_5$. Similarly also with the hydrate **barium molybdenum hemipentoxide,** $BaMo_2O_5.3H_2O$, and the anhydrous $BaMo_2O_5$.

J. J. Berzelius[5] obtained what he regarded as **molybdenum pentitatetradecaoxide,** Mo_5O_{14}, or $MoO_2.4MoO_3$, by heating molybdenum or one of the lower oxides in air for a short time. C. F. Rammelsberg obtained the *hexahydrate* by allowing an aq. soln. of molybdic acid to stand in contact with reduced molybdenum for some days, and then shaking up the filtered, blue liquid with an excess of molybdenum for some days. M. Guichard said that this compound is best obtained by mixing cold, dil. hydrochloric acid soln. of molybdenum dioxide and ammonium molybdate; the hydrochloric acid should be that of sp. gr. 1·18 diluted with 9 parts of water, this bringing about complete precipitation without decomposition. A more conc. acid decomposes the oxide. The product thus obtained is nearly insoluble in cold water, although that prepared by C. F. Rammelsberg, by precipitation at 50°, is easily soluble; an aq. soln. of the oxide is readily obtained by leaving molybdenum trioxide and metallic molybdenum in contact in water. The oxide obtained by precipitation is a dark blue powder of sp. gr. 3·6 at 18°; by the evaporation of its soln., it is obtained in vitreous, faceted fragments, which yet are not truly crystalline. It dissolves in water at 50°, but is insoluble in sat. soln. of ammonium, sodium and calcium chlorides, and potassium iodide and nitrate; sodium and magnesium sulphate do not alter its solubility. It dissolves in 95 per cent. alcohol, although it is insoluble in most organic solvents. When heated in vacuo or an inert gas, it loses part of its water at 100°, and the rest near a red-heat, a non-homogeneous mixture of molybdenum dioxide and trioxide being formed. Hydrogen ultimately reduces it to the metal; chlorine yields the volatile oxychloride, MoO_2Cl_2, and molybdenum trioxide. Contrary to J. J. Berzelius' statement, it slowly oxidizes in the air, and at a red-heat oxygen rapidly converts it into the trioxide. Gaseous hydrogen chloride at a red-heat and superheated steam decompose it, giving mixed dioxide and trioxide; gaseous ammonia gives initially the same result, but at a red-heat reduces the oxides to the metal. Acetic acid does not affect it; by conc. hydrochloric acid, it is dissolved to a yellowish-red soln. of molybdenum tetrachloride, but the action is a reversible one, since, on diluting with water, the blue oxide is precipitated. With sulphuric acid, a like result is obtained. K. von der Heide and K. A. Hofmann reported **ammonium molybditetramolybdate,** $(NH_4)_2O.MoO_2.4MoO_3.6H_2O$, to be formed by heating an aq. soln. of ammonium molybdate with half its weight of hydroxylamine hydrochloride on the water-bath until the orange precipitate which is at first formed is dissolved, and a greenish-brown soln. is obtained; this soln. is then rapidly filtered, protected from access of air, and allowed to cool. The compound separates in dark red crystals belonging to the triclinic system; dissolves gradually in water with a reddish-yellow coloration; and is fairly stable. It gradually reduces Fehling's soln. in the cold and quickly when heated. With copper sulphate, it gives a beautiful, blue coloration; with mercurous and mercuric salts, a flesh-coloured precipitate; with lead nitrate, a yellowish-white precipitate; and with potassium thiocyanate, an intense red coloration. It is gradually decomposed by dil. acids, and it reduces ammoniacal silver soln. with the separation of metallic silver. Other ammonia derivatives with the lower oxides of molybdenum, analogous to the chromammine bases, could not be prepared.

P. Klason [6] obtained a soluble oxide $Mo_{20}O_{41}.21H_2O$, or $Mo_2O_5.18MoO_3.21H_2O$, by exposing an aq. soln. of ammonium molybdenyl chloride to air. The solid furnishes a blue soln. with water, and it is precipitated by adding ammonium chloride. According to W. Muthmann, the oxide Mo_5O_{12}, first described by N. J. Berlin, is obtained by heating a mixture of ammonium molybdate with twice its weight of molybdenum trioxide. The product is repeatedly extracted with ammonia, and finally with conc. hydrochloric acid to remove a compound of molybdenum and nitrogen. This oxide is not attacked by alkali-lye, but it dissolves in warm conc. sulphuric acid, forming a green soln., which easily parts with sulphur dioxide, and turns blue. Nitric acid, aqua regia, and chlorine-water convert Mo_5O_{12} into the trioxide. H. O. Schulze obtained Mo_4O_{11}, or $Mo_2O_3.2MoO_4$, by heating a mixture of potassium iodide and molybdenum trioxide; G. Bailhache, the *hexahydrate* by the action of barium molybdate on the oxysulphate, $Mo_2O_5.2SO_4$; G. Bailhache, $Mo_{20}O_{57}.18H_2O$, or $2Mo_2O_3.2Mo_7O_{24}.18H_2O$, by the action of barium 3 : 7-molybdate on $Mo_2O_5.2SO_4$; A. Junius, Mo_7O_{20}, by the electrolysis of a hydrochloric acid soln. of ordinary ammonium paramolybdate, or of sodium molybdate; and P. Klason, $Mo_{26}O_{77}.24H_2O$, or $Mo_2O_5.24MoO_3.24H_2O$, by exposing an aq. soln. of ammonium molybdenyl chloride to oxidation by air for several months. There is nothing to show that these products are not merely arbitrary intermediate stages in the reduction of molybdenum trioxide. Some suggestions have been made for the use of the blue oxides of molybdenum as pigments—*vide supra*, the uses of molybdenum. Hydrosols of *molybdenum blue* were found by P. Lal and P. B. Ganguly to be coagulated by ultra-violet light.

REFERENCES.

[1] F. Ullik, *Sitzber. Akad. Wien*, **55**. 767, 1867; *Liebig's Ann.*, **144**. 204, 320, 1867; D. K. Tuttle, *Miscellaneous Chemical Researches*, Göttingen, 1857; *Liebig's Ann.*, **101**. 285, 1857; W. Muthmann, *Ber.*, **20**. 989, 1887; *Ueber niedere Oxyde des Molybdäns*, München, 1886; *Liebig's Ann.*, **238**. 108, 1887; G. Rauter, *ib.*, **270**. 236, 1892; N. Parravano and G. Malquori, *Gazz. Chim. Ital.*, **58**. 279, 1928; W. Püttbach, *Ueber Molybdänchloride*, Elberfeld, 1878; *Liebig's Ann.*, **201**. 125, 1880; G. Krüss, *ib.*, **225**. 1, 1884; H. Buff, *ib.*, **110**. 275, 1859; L. P. Liechti and B. Kempe, *ib.*, **169**. 344, 1873; H. Rose, *Pogg. Ann.*, **75**. 319, 1847; C. F. Rammelsberg, *ib.*, **127**. 282, 1866; J. Reich, *Elektrolytische Reduktion von Nitrokörpern mit Molybdän als Wasserstoffübertrager*, J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817; *Pogg. Ann.*, **4**. 153, 1825; **6**. 331, 369, 1826; **7**. 261, 1826; *Ann. Chim. Phys.*, (2), **17**. 5, 1821; L. F. Svanberg and H. Struve, *Svenska Akad. Handl.*, **1**. 9, 1848; *Journ. prakt. Chem.*, (1), **44**. 257, 1848; *Phil. Mag.*, (3), **33**. 409, 524, 1848; C. F. Bucholz, *Scherer's Journ.*, **9**. 485, 1903; *Gehlen's Journ.*, **4**. 598, 1803; *Phil. Mag.*, **16**. 193, 1803; *Nicholson's Journ.*, **20**. 121, 188, 253, 1808; *Journ. Mines*, **18**. 241, 1808; H. Debray, *Compt. Rend.*, **45**. 1020, 1857; B. A. Dima, *ib.*, **157**. 590, 1913; M. Guichard, *Ann. Chim. Phys.*, (7), **23**. 504, 1901; *Recherches sur les oxydes, les sulfures, et les iodures de*

molybdène, Paris, 22, 1900 ; C. Friedheim and M. K. Hoffmann, *Ber.*, **35**. 791, 1902 ; M. K. Hoffmann, *Zur Analyse von niederen Molybdänoxydverbindungen und Beiträge zur Chemie der Salze derselben*, Bern, 8, 1903 ; E. Uhrlaub, *Pogg. Ann.*, **101**. 605, 1857 ; *Die Verbindungen einiger Metall mit Stickstoff*, Göttingen, 20, 1859 ; L. A. Munro, *Proc. Nova Scotia Inst.*, **16**. 9, 1927 ; L. Ott, *Elektrolyse geschmolzener Molybdate und Vanadate*, München, 23, 1911 ; W. M. Dehn and B. B. Wilcox, *Amer. Chem. Journ.*, **35**. 29, 1906 ; A. Michael and A. Murphy, *ib.*, **44**. 365, 1910 ; O. W. Gibbs, *ib.*, **17**. 167, 1895 ; W. G. Mixter, *Amer. Journ. Science*, (4), **29**. 488, 1910 ; A. Vandenberghe, *Bull. Acad. Belg.*, (3), **30**. 127, 1896 ; S. Stevanovic, *Zeit. Kryst.*, **37**. 254, 1903 ; F. Mauro and R. R. Panebianco, *Gazz. Chim. Ital.*, **11**. 501, 1881 ; *Atti Accad. Lincei*, (3), **9**. 418, 1881 ; E. Péchard, *Ann. Chim. Phys.*, (6), **28**. 537, 1893 ; *Compt. Rend.*, **118**. 804, 1894 ; **143**. 744, 1907 ; G. Chaudron, *ib.*, **170**. 182, 1920 ; F. J. Faktor, *Pharm. Post*, **34**. 485, 1901 ; G. Martin, *Chem. News*, **92**. 185, 1905 ; W. Skey, *ib.*, **16**. 201, 1867 ; **17**. 150, 184, 1868 ; A. Rogers and F. H. Mitchell, *Journ. Amer. Chem. Soc.*, **22**. 350, 1900 ; E. F. Smith and O. L. Shinn, *ib.*, **16**. 569, 1894 ; *Zeit. anorg. Chem.*, **7**. 47, 1894 ; C. Engler and L. Wöhler, *ib.*, **29**. 1, 1901 ; O. L. Shinn, *The Atomic Mass of Tungsten—Molybdenum Dioxide and Silver Salts*, Philadelphia, 1896 ; E. Friederich and L. Sittig, *Zeit. anorg. Chem.*, **145**. 127, 1925 ; E. Friederich, *Zeit. Physik*, **31**. 813, 1925 ; S. Berkman and H. Zocher, *Zeit. phys. Chem.*, **124**. 318, 1926 ; C. Paal and H. Büttner, *Ber.*, **48**. 220, 1915 ; C. Paal and G. Brunjes, *ib.*, **47**. 2214, 1914 ; P. Klason, *ib.*, **34**. 148, 1901 ; E. Wedekind and C. Horst, *ib.*, **48**. 105, 1915 ; N. J. Berlin, *Journ. prakt. Chem.*, (1), **49**. 444, 1850 ; H. Freundlich and W. Leonhardt, *Koll. Beihefte*, **7**. 172, 1915 ; E. J. Millard, *Pharm. Journ.*, (3), **19**. 585, 1889 ; C. Bärwald, *Beiträge zur Kenntniss Molybdäns*, Berlin, 1885 ; *Ber.*, **17**. 1206, 1884 ; W. R. E. Hodgkinson and F. K. S. Lowndes, *Chem. News*, **58**. 309, 1888 ; L. Pauling, *Journ. Amer. Chem. Soc.*, **49**. 765, 1927 ; G. Reissaus, *Metall Erz*, **21**. 118, 1924 ; E. Müller, *Zeit. Elektrochem.*, **33**. 182, 1927 ; E. Müller and H. Möllering, *Zeit. anorg. Chem.*, **141**. 111, 1924 ; G. Unger, *Mangananalytische Bestimmung von reduzierten Molybdänlösungen unter Zuhilfenahme der Potentiometrie*, Dresden, 1926 ; E. Fricke, *Ueber die elektrolytische Reduktion von Molybdänlösungen und die aus reduzierten wässerigen Lösungen zu gewinnenden Salze des Molybdäns niederer Wertigkeitsstufen*, Dresden, 1923 ; M. L. Huggins, *Phys. Rev.*, (2), **21**. 719, 1923 ; V. M. Goldschmidt, T. Barth, D. Holmsen, G. Lunde and W. Zachariasen, *Skrift. Nordske Akad.*, **1**, 1926 ; J. Vrede, *Phys. Zeit.*, **31**. 323, 1930 ; J. Duclaux and R. Titéica, *Rev. Gén. Colloid.*, **7**. 289, 1929 ; W. Biltz, *Zeit. anorg. Chem.*, **193**. 321, 1930.

[2] H. Höfer, *Neues Jahrb. Min.*, 566, 1871 ; *Die Mineralien des Kärtens*, Klagenfurt, 42, 1870 ; E. Dittler, *Centr. Min.*, 689, 1922 ; 705, 1923 ; J. J. Berzelius, *Akad. Handl. Stockholm*, 145, 1825 ; *Ann. Phil.*, **11**. 235, 1926 ; *Edin. Journ. Science*, **4**. 133, 1826 ; *Pogg. Ann.*, **6**. 331, 369, 1826 ; C. F. Rammelsberg, *ib.*, **127**. 290, 1866 ; F. L. Hess, *Bull. U.S. Geol. Sur.*, 750, 1923 ; W. Muthmann, *Liebig's Ann.*, **238**. 108, 1887 ; F. Cornu, *Koll. Zeit.*, **4**. 190, 1909 ; *Tschermak's Mitt.*, (2), **28**. 196, 1909 ; W. T. Schaller, *Journ. Washington Acad.*, **7**. 417, 1917 ; *Chem. News*, **116**. 94, 1917 ; C. W. Greenland, *Amer. Min.*, **2**. 113, 122, 134, 145, 1917 ; H. F. Yancey, *Chem. Met. Eng.*, **19**. 186, 1918 ; A. Himmelbauer, *Fortschr. Min.*, **3**. 39, 1913.

[3] A. Dumansky, *Zeit. Koll.*, **7**. 20, 1910 ; W. Biltz, *Ber.*, **35**. 4431, 1902 ; **37**. 1095, 1766, 1904 ; *Nachr. Gött.*, 1, 1904 ; W. Biltz and W. Geibel, *ib.*, 141, 1906 ; C. Winssinger, *Bull. Acad. Belg.*, (3), **15**. 390, 1888 ; J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817 ; *Pogg. Ann.*, **4**. 153, 1825 ; **6**. 331, 369, 1826 ; **7**. 261, 1826 ; *Ann. Chim. Phys.*, (2), **17**. 5, 1821 ; C. F. Bucholz, *Scherer's Journ.*, **9**. 485, 1803 ; *Gehlen's Journ.*, **4**. 598, 1803 ; *Phil. Mag.*, **16**. 193, 1803 ; *Nicholson's Journ.*, **20**. 121, 188, 253, 1803 ; *Journ. Mines*, **18**. 241, 1808 ; O. Maschke, *Zeit. anal. Chem.*, **12**. 384, 1873 ; L. Schönn, *ib.*, **9**. 41, 330, 1870 ; G. Marchetti, *Zeit. anorg. Chem.*, **19**. 391, 1899 ; C. F. Rammelsberg, *Pogg. Ann.*, **127**. 281, 1866.

[4] P. Klason, *Ber.*, **34**. 148, 153, 158, 1901 ; E. F. Smith and V. Oberholtzner, *Zeit. anorg. Chem.*, **4**. 236, 1893 ; E. Friederich and L. Sittig, *ib.*, **145**. 127, 1925 ; E. Friederich, *Zeit. Physik*, **31**. 813, 1925 ; S. Ghosh and N. R. Dhar, *Koll. Zeit.*, **41**. 229, 1927 ; C. F. Rammelsberg, *Pogg. Ann.*, **127**. 290, 1866 ; E. Péchard, *Ann. Chim. Phys.*, (6), **28**. 537, 1893 ; J. Reich, *Elektrolytische Reduktion von Nitrokörpern mit Molybdän als Wasserstoffübertrager*, München, 1910 ; Badische Anilin- und Sodafabrik, *German Pat.*, *D.R.P.* 246377, 1910 ; J. N. Pearce and A. M. Alvarado, *Journ. Phys. Chem.*, **29**. 256, 1925 ; G. A. Barbieri, *Atti Accad. Lincei*, (5), **25**. i, 775, 1916 ; J. N. Pearce and A. M. Alvarado, *Journ. Phys. Chem.*, **29**. 256, 1925 ; G. Reissaus, *Metall Erz.*, **21**. 118, 1924 ; E. Müller, *Zeit. Elektrochem.*, **33**. 182, 1927 ; E. Müller and H. Möllering, *Zeit. anorg. Chem.*, **141**. 111, 1924 ; F. Mawroff and M. Nikoloff, *ib.*, **92**. 135, 1915 ; G. Unger, *Manganalytische Bestimmung von reduzierten Molybdänlösungen unter Zuhilfenahme der Potentiometrie*, Dresden, 1926 ; E. Fricke, *Ueber die elektrolytische Reduktion von Molybdänlösungen und die aus reduzierten wässerigen Lösungen zu gewinnenden Salze des Molybdäns niederer Wertigkeitsstufen*, Dresden, 1923 ; P. Sabatier and A. Mailhe, *Ann. Chim. Phys.*, (8), **20**. 289, 1910 ; *Compt. Rend.*, **152**. 1212, 1911 ; H. Debray, *ib.*, **45**. 1020, 1857 ; M. Guichard, *ib.*, **129**. 722, 1899 ; **131**. 389, 419, 1900 ; W. Wardlaw and F. H. Nicholls, *Journ. Chem. Soc.*, **127**. 1487, 1925 ; E. Newbery and J. N. Pring, *Proc. Roy. Soc.*, **92**. A, 276, 1916 ; J. Vrede, *Phys. Zeit.*, **31**. 323, 1930 ; W. Meissner, *Zeit. Ges. Kälte-Ind.*, **37**. 174, 1930 ; A. Schulze, *Zeit. Metallkunde*, **22**. 311, 1930.

[5] J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817 ; *Pogg. Ann.*, **4**. 153, 1825 ; **6**. 313, 369, 1826 ; **7**. 261, 1826 ; *Ann. Chim. Phys.*, (2), **17**. 5, 1821 ; C. F. Rammelsberg, *Pogg. Ann.*, **127**. 281, 1866 ; M. Guichard, *Compt. Rend.*, **131**. 389, 419, 1900 ; *Bull. Soc. Chim.*, (4), **1**. 446, 1907 ; *Ann. Chim. Phys.*, (7), **23**. 498, 1901 ; *Recherches sur les oxydes, les sulfures, et les iodures de molybdène*, Paris, 1900 ; K. von der Heide and K. A. Hofmann, *Zeit. anorg. Chem.*, **12**. 277, 1896 ;

K. von der Heide, *Ueber Verbindungen der niederen Molybdänoxyde und -sulfide mit Ammoniak und Cyankalium*, München, 1897.

[6] P. Klason, *Ber.*, **34**. 148, 153, 158, 1901 ; W. Muthmann, *ib.*, **20**. 989, 1887 ; *Liebig's Ann.*, **238**. 108, 1887 ; *Ueber niedere Oxyde des Molybdäns*, München, 1886 ; N. J. Berlin, *Journ. prakt. Chem.*, (1), **49**. 444, 1850 ; H. O. Schulze, *ib.*, (2), **21**. 440, 1880 ; A. Junius, *Zeit. anorg. Chem.*, **46**. 428, 1905 ; *Beiträge zur Kenntnis der Molybdate*, Berlin, 1905 ; G. Bailhache, *Compt. Rend.*, **133**. 1210, 1901 ; C. F. Rammelsberg, *Pogg. Ann.*, **127**. 290, 1866 ; J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817 ; *Pogg. Ann.*, **4**. 153, 1825 ; **6**. 331, 369, 1826 ; **7**. 261, 1826 ; *Ann. Chim. Phys.*, (2), **17**. 5, 1821 ; P. Lal and P. B. Ganguly, *Journ. Indian Chem. Soc.*, **7**. 513, 1930.

§ 10. Molybdenum Trioxide and its Hydrates

D. L. G. Karsten[1] recognized a yellow earth associated with the molybdenite at Nummedalen, Norway, as a mineral species which he called **molybdic ochre**—*Wasserbleiocker*, and *Molybdänocker ;* J. F. L. Hausmann said that the essential constituent is molybdenum oxide; and J. J. Berzelius, and F. von Kobell, molybdenum trioxide. R. P. Greg and W. G. Lettsom called it *molybdin*, and A. Breithaupt, **molybdite.** It appears as an oxidation product of molybdenite. W. T. Schaller represented the composition of samples from California; Westmoreland, New Hampshire; Telluride, Colorado; and Renfrew, Ontario, by $Fe_2O_3.3MoO_3.7\frac{1}{2}H_2O$—*vide infra*, ferric molybdate; and F. N. Guild, that of a sample from Santa Rita Arizona, by $Fe_2O_3.3MoO_3.7H_2O$. D. D. Owen had previously suggested that the molybdic ochre from Nevada City, California, is a ferric molybdate, but F. A. Genth regarded this sample as a molybdic ochre mixed with limonite—P. P. Pilipenko called the ferruginous mineral ferrimolybdite—*vide infra*, ferric molybdate.

Occurrences have been noted at Caldbeck Fell, Cumberland, by R. P. Greg and W. G. Lettsom ; at Mount Coryby and Tulloch, Scotland, by R. P. Greg and W. G. Lettsom, and M. F. Heddle ; at Creux and Vaubry, Saint-Léonard, Vilati, etc., France, by A. Lacroix ; near Porto, Portugal, by C. F. A. Tenne and S. Calderon ; in Novara, and Sardinia, Italy, by W. P. Jervis, and D. Lovisato ; in Glarus, Switzerland, by E. Stöhr, and G. A. Kenngott ; at Pfitsch, Tyrol, by C. C. von Leonhard, and J. F. L. Hausmann ; at Berggiesthübel, and Altenberg, Saxony, by A. Breithaupt, and A. Frenzel ; at Schlaggenwald, by V. von Zepharovich, at Nummedalen, Norway, by D. L. G. Karsten ; at Linnäs, and Bispberg, Sweden, by C. C. von Leonhard, W. Hisinger, and J. F. L. Hausmann ; Pitkäranta, Finland, by A. Breithaupt ; on the Adun-Chalon Mountains, Siberia, by J. D. Dana ; in Victoria, and Tasmania, by G. H. F. Ulrich, and W. F. Petterd ; in St. Fernando, Chile, by I. Domeyko ; in Huaylas, Peru, by A. Raimondi ; in Mexico, by C. F. de Landero ; in Nevada, Texas, Georgia, North Carolina, Pennsylvania, and New Hampshire, United States, by D. D. Owen, F. A. Genth, W. E. Hidden and J. B. Mackintosh, W. T. Schaller, F. N. Guild, T. S. Hunt, P. Groth, and J. D. Dana ; and in Quebec, and Ontario, Canada, by G. C. Hoffmann.

The end-products of the oxidation of molybdenum, and, naturally, of the lower oxides, is **molybdenum trioxide,** MoO_3. J. J. Berzelius obtained the trioxide by roasting molybdenum sulphide in air. According to H. V. Regnault,[2] it is formed when steam acts on the red-hot metal, or on a lower oxide ; and, according to J. von Liebig, when heated potassium hydroxide acts on the metal—in that case, hydrogen is evolved. J. J. Berzelius obtained the trioxide by the action of an excess of nitric acid on molybdenum or its lower oxides, and either evaporating the soln. to dryness and igniting, or allowing the soln. to evaporate spontaneously. C. W. Scheele also obtained molybdenum trioxide by the action of nitric acid on molybdenite. The extraction of molybdates from molybdenite or wulfenite has been previously described, and J. J. Berzelius, and G. C. Wittstein obtained molybdenum trioxide from the ammonium salt by heating it in an open crucible at a temp. below the fusion point. In the roasting of ammonium molybdate the residual molybdenum trioxide is more or less reduced, and L. Ott, and W. Muthmann said that it should be heated to dull redness for 4 or 5 hrs. in a current of oxygen. R. Stierlin obtained the trioxide by sublimation from ammonium phosphatomolybdate ; and F. Elias heated molybdenum phosphate with a soln. of phosphoric acid in a sealed tube at 140° and obtained microcrystalline molybdenum trioxide.

The purification of molybdic acid is described in connection with the recovery of molybdenum from laboratory residues where the trioxide is associated with more or less phosphoric acid. P. Klason found commercial molybdenum trioxide of the composition $NH_3.3MoO_3.\frac{1}{2}H_2O$. H. Debray found commercial molybdenum trioxide associated with sodium salts and sulphuric acid. He purified it by admixture with ammonium chloride; and washing with water, and oxidizing the product by roasting it in air, or by treatment with nitric acid. The purification of the trioxide by sublimation frees it from metallic impurities, tungsten trioxide, silica, and phosphates. L. Rolla and G. Piccardi, for instance, purified the trioxide by sublimation in a current of air in a quartz tube. According to L. Wöhler and W. Engels, the precipitation which occurs when soln. of molybdates are acidified is due to the presence of tungstates. The readiness with which precipitation takes place is dependent on the proportion of tungstic acid present, and when this is present in very small amount, the temp. may be raised to nearly 100° before a precipitate is obtained. The precipitation is primarily due to the tungstic acid in the soln., and when this separates out, molybdic acid is simultaneously removed from the soln. A. Arnfeld observed that commercial molybdenum trioxide contains some of the lower oxides which are converted into the trioxide by roasting at a red-heat. In order to prepare the trioxide free from ammonia, M. Liebert boiled 50 grms. of ammonium molybdate in 100 c.c. of aqua regia until the liquid no longer gave a sign of the presence of ammonia when tested with Nessler's reagent. The product was then evaporated a number of times with nitric acid, and finally dried at 180°. W. D. Collins and co-workers discussed the impurities in commercial molybdic acid. The so-called " molybdic acid, 85 per cent." consists largely of ammonium molybdate.

The analyses of J. J. Berzelius,[3] J. B. A. Dumas, H. Debray, C. F. Bucholz, L. Ott, K. Seubert and W. Pollard, C. F. Rammelsberg, J. H. Müller, and A. Vandenberghe, are in agreement with the formula MoO_3. From the effect of molybdenum trioxide on the b.p. of sulphuric acid, E. Beckmann calculated the mol. wt. to be in accord with the formula $(MoO_3)_2$, or Mo_2O_6. Molybdenum trioxide has a platy or talcose structure, and it is colourless and non-pleochroic. The mass which has been fused is greyish- or yellowish-white with a radiating fibrous structure, whilst the sublimed trioxide furnishes colourless, transparent, thin plates, or needles which, according to A. E. Nordenskjöld, belong to the rhombic system; the **crystals** have the axial ratios $a:b:c=0.3872:1:0.4792$. P. Groth said that the crystals are probably isomorphous with those of tungsten trioxide. The (100)-, (010)-, and (001)-**cleavages** are distinct. The **optical character** is positive. A. des Cloizeaux gave for the **optic axial angles** at 13°, $2H_0=117°\,15'$ for red-light, 119° 33′ for yellow-light, and 127° for blue-light. A. Lacroix found the natural crystals from Corsica to be pleochroic—*a* and *b* are pale yellow, whilst *c* is nearly black. P. Niggli discussed the electronic structure; and H. E. Buckley, the effect of molybdates on the growth of crystals of sodium chlorate.

A. Breithaupt gave 4·49 to 4·50 for the **specific gravity** of molybdic ochre; T. Bergman, 3·46 for molybdenum trioxide; V. Eggertz, 4·5 for the sublimed oxide; E. Wedekind and C. Horst, 4·50 at 19·5°; and A. Safarik, 4·39 at 21° for the trioxide which had been fused. W. Biltz, D. Balareff, and C. del Fresno studied the mol. vol. The hardness of molybdic ochre is 1 to 2. J. Maydel discussed the **specific heat.** T. Carnelley gave $759°\pm2°$ for the **melting point** of the trioxide; F. Hoermann, and F. M. Jäger and H. C. Germs, 795°. E. Groschuff said that it melts without decomposition at 791°. When molybdenum trioxide is heated, it becomes lemon-yellow, and the original colour is restored on cooling. W. D. Bancroft and H. B. Weiser observed that when the trioxide is introduced in the oxyhydrogen flame, the flame gives a bright, lustrous, metallic mirror on a cold surface. It fuses at a red-heat to a brownish-yellow liquid. C. Zenghelis obtained evidence of a slight volatilization at ordinary temp. In covered vessels, it volatilizes at a high temp. only, but when exposed to air, even at its m.p., it volatilizes forming white fumes which condense above the fused mass to form a crystalline sublimate. E. Groschuff said that sublimation begins in the vicinity of the m.p. P. H. M. P. Brinton and A. E. Stoppel found that the trioxide is non-volatile below 500°, and volatilizes only slightly between 500° and 600°. G. Merz, and C. F. Plattner noticed that the trioxide volatilizes before the blowpipe flame which is coloured a greenish-yellow; W. R. Mott made some observations on the volatilization of the trioxide in the electric arc. A. A. Read said that the trioxide gives off oxygen at 1750°; and K. W. G. Kastner, that it is reduced to metal in the oxyhydrogen blowpipe flame. W. G. Mixter gave for the **heat of formation** when the metal is oxidized by sodium dioxide, $(Mo,3O)=181{\cdot}5$ Cals. at constant vol., or $(MoO_2,O)=38{\cdot}7$ Cals. S. M. Delépine gave $(Mo,3O)=166{\cdot}14$ Cals. at constant vol., and 167·00 Cals. at constant press.; W. Lederer gave 168·675 Cals. at constant vol.; J. E. Moose and S. W. Parr, 1829 cals. per gram. The subject was discussed by A. Berkenheim.

R. Stierlin referred to *das wunderbare Farbenspiel* which occurs when the crystals are examined by polarized light. E. L. Nichols and B. W. Snow found the fractional **reflecting power,** R, for light of wave-length, λ, to be:

λ	7530	6685	6080	5570	4920	4685	4500	4340
R 25°	—	0·695	0·613	0·517	0·309	0·139	0·068	0·045
R 275°	0·720	0·596	0·465	0·335	0·101	—	0·040	—

The reflected light is partly made up of mainly white light reflected from the surface, and partly, of light reflected from the interior, and this determines the colour of the reflected light. D. Gernez showed that molybdic acid, and the alkali molybdates, though optically inactive, can augment the optical activity of other substances—*e.g.* tartaric acid. L. W. Andrews examined the action with malic acid; and C. N. Riiber and J. Minsaas, with galactose. G. A. Dima studied the **photoelectric effect.** T. W. Case said that no electrical conductivity is to be observed when molybdenum trioxide is exposed to light. J. M. Eder, unlike T. L. Phipson, observed that a sulphuric acid soln. of molybdic acid is not reduced by exposure to light provided organic matter be absent. M. Jungck observed that the soln. of ammonium molybdate used in analytical chemistry suffers photolysis. R. Robl observed but a faint luminescence in ultra-violet light; E. Tiede and A. Schleede, the phosphorescence of molybdenum trioxide in active nitrogen; J. Ewles, the cathode luminescence, but no ultra-violet fluorescence with X-rays was observed by J. O. Perrine; H. T. Meyer, the K-series of the X-ray spectrum; and H. Nisi, the **Raman effect.**

F. Beijerinck found that molybdic ochre is a non-conductor of electricity; and T. W. Case observed that the trioxide is also a non-conductor, whilst L. Bleekrode said that it is a good conductor. A. Miolati studied the **electric conductivity** of mixtures containing molybdic acid. E. Friederich calculated $7{\cdot}8\times10^{10}$ ohms for the resistance of a metre wire 1 sq. mm. cross-section. H. Buff, and M. Guichard found that molten molybdenum trioxide is a good conductor, and on **electrolysis** furnishes crystals of the tritoctoxide at the cathode; K. W. G. Kastner obtained the metal. T. de Grotthus observed that when a soln. of molybdic acid in sulphuric acid is electrolyzed, the liquid about the cathode is coloured blue. G. Gore made a similar observation with respect to soln. in hydrofluoric acid; and J. Terwelp found that water with molybdenum trioxide in suspension becomes blue about the cathode when it is electrolyzed. L. Schicht also noticed the blue soln. formed when a soln. of ammonium molybdate is electrolyzed, and J. G. Gahn observed the separation of what he thought to be molybdenum at the cathode. G. Gore obtained a black deposit on electrolyzing fused molybdic acid. E. Péchard found that the electrolysis of a soln. of ammonium molybdate in hydrochloric or oxalic acid gives a soln. of molybdenum dioxide, which, with strongly ammoniacal soln., gives a deposit of $MoO_2.H_2O$ on the cathode. A. Chilesotti found that the electrolysis of a feebly acid soln. of molybdic acid in sulphuric acid gives a quantitative separation of molybdenum at the mercury cathode, but not so with a $3N$-H_2SO_4 soln. The electrolysis of a hydrochloric acid soln. of molybdenum trioxide or of a soln. of ammonium molybdate in dil. sulphuric acid using a mercury cathode gives a soln. of tervalent molybdic chloride or sulphate. J. Férée also obtained molybdenum amalgam at the mercury cathode when a soln. of molybdic acid in hydrofluoric acid was electrolyzed—current density 5 amp. per sq. cm. The electrolysis of these soln. was also studied by R. E. Myers, E. F. Smith and co-workers, and A. Chilesotti and A. Rozzi. According to A. Chilesotti, when a soln. of molybdic acid is electrolyzed, part of the hydrogen at the cathode reduces the molybdic acid, and part escapes as a gas, so that the current efficiency for any period can be calculated by comparing the amounts of hydrogen produced in the cell, and in a voltameter in the same circuit. When the reduction is completed, the current efficiency is zero. With a soln. containing 3·5 per cent. of molybdenum trioxide in $9N$-HCl, and a mercury cathode, and high current densities, a large fraction of the current is employed in liberating hydrogen, but the time required for complete reduction is short. Increasing the conc. of the molybdic acid increases the current efficiency; with the $9N$-HCl, the current efficiency is at first 100, it afterwards falls regularly to zero. With $4N$-acid, the curve again begins at 100, but soon falls very rapidly to about 10 and then rises slowly to a maximum at 29, thereafter falling to zero. With more dil. acid, the curve follows a similar course, but the maximum occurs sooner and at a much higher value of the current efficiency. The probable explanation is that a film of oxide is first formed on the cathode, which acts as a diaphragm and prevents reduction; later this film is dissolved or reduced to metal and metallic molybdenum amalgam is formed on the surface of the cathode, the reducing action of the amalgam being much greater than that of the mercury alone. It is known that molybdenum amalgam is formed in presence of dil. acid, but not in conc. acid. Rise of temp. increases the current efficiency considerably. The material of the cathode has a greater effect on the current efficiency. Using a soln. of 3·5 per cent. of molybdenum trioxide in $4N$-HCl, a current density of 0·042 amp. per sq. cm. at 10°–20°, the average current efficiencies were, with platinized platinum, 10·6 per cent., mercury, 18·9 per cent., smooth platinum, 51·7 per cent., tin, 66·9 per cent., and lead, 74·5 per cent. In $9N$-HCl, tin gave the best result, lead and platinum slightly worse results, and mercury was worst of all. The behaviour of these metals has obviously no connection with the overvoltage required to liberate hydrogen in their surfaces; rather would it appear to be connected with their solubility, both lead and tin being found in soln. after the electrolysis, which was not the case with platinum and mercury. The molybdic acid is always reduced to tervalent molybdenum compounds except when a platinized platinum cathode is used; in this case, the reduction stops at the quinquevalent stage. Soln. in sulphuric and oxalic acids gave similar results, the tin cathode being insoluble in the oxalic acid soln., and the lead cathode insoluble in the sulphuric acid soln. gave results similar to those obtained with platinum.

A. Chilesotti also measured the **potential difference** between platinum and the soln. at different stages of the reduction. It was found that in all cases the same general result was obtained. The potential difference increases slowly as the reduction proceeds, until the whole of the molybdenum is in the quinquevalent condition; it then rises very suddenly to a higher value, after which it again increases slowly until the molybdenum is almost reduced to the tervalent state, when a further rather sudden increase occurs. During the first stage of the reduction, the potential is doubtless conditioned by the process $MoO_4''+8H^{\cdot}+\oplus =Mo^{\cdot\cdot\cdot\cdot\cdot}+4H_2O$; during the second stage, the main change is probably the reduction of quinquevalent to tervalent molybdenum. The final increase is due possibly to the formation of bivalent molybdenum ions. With regard to colour, the soln. in $7N$- to $9N$-HCl first becomes emerald-green owing to the formation of the complex compound of the oxychloride, $MoOCl_3$; they then become brown and finally orange-red, and contain complex compounds of the formula ($MoCl_3,nHCl$). The soln. in more dil. hydrochloric acid change, when the reduction is almost complete, from a brownish-red colour to a deep olive-green colour. The green soln. are unstable; they decompose water, taking up oxygen and becoming brownish-red again. Both the red and the green soln. contain molybdenum trichloride, and it is supposed that they are related in the same way as the green and violet soln. of chromic chloride. The soln. in sulphuric acid behave similarly. The change from one modification to the other is due possibly to the presence of traces of molybdenum dichloride. J. Terwelp found that the electrolysis of 10 per cent. soln. of $(NH_4)_6Mo_7O_{24}.4H_2O$, and of 2 to 10 per cent. soln. of normal sodium molybdate without diaphragms gives only a small cathodic deposit of indefinite composition; with a diaphragm, the former salt gives with a small anode current density a deposit of $(NH_4)_2Mo_7O_{22}.8H_2O$, and a yellow anode liquid of molybdic acid. L. Ott found that the electrolysis of fused sodium or barium polymolybdate gives molybdenum dioxide, whilst with fused normal sodium molybdate oxygen is given off at the anode and a pulverulent mixture of the lower oxides is deposited. L. Ott also studied the electrolysis of soln. of molybdenum trioxide, and of the sodium molybdate. According to F. Förster and co-workers, the fact that soln. of molybdic acid in dil. hydrochloric acid can only be reduced to the quinquevalent stage, whilst soln. in more conc. hydrochloric acid can be reduced electrolytically to the tervalent stage, is explained by assuming that the next stage to quinquevalent molybdenum is $Mo^{\cdot\cdot\cdot}$-ions, which in the presence of a high conc. of Cl'-ions immediately form complex ions and the static potential of the soln. is reduced below that necessary for the generation of hydrogen from platinized platinum electrodes. If the conc. of chloride-ions is low, however, comparatively few complex ions are formed, and the static potential of the soln. remains higher than that necessary for the evolution of hydrogen. If polished platinum electrodes are used, however, owing to the much higher potential necessary for the evolution of hydrogen, the tervalent stage can be reached even in dil. hydrochloric acid soln. The electrolytic reduction of molybdenum shows changes of potential parallel with those occurring in vanadium and titanium soln. under similar conditions. L. Rolla and G. Piccardi found that molybdenum trioxide, completely freed from bases by sublimation, has an **electro-affinity** of 2·73 volts, calculated on the assumption that no dissociation occurs at 1970° K.

According to H. T. S. Britton and W. L. German, the **electrometric titration** curve of soln. of sodium molybdate with hydrochloric acid shows an inflexion at $p_H=4{\cdot}8$, corresponding with the formation of $3Na_2O.7MoO_3$ (or $5Na_2O.12MoO_3$). By boiling the soln. or ageing it prior to measuring the p_H-curve furnishes a sharper inflexion corresponding with $Na_2O.4MoO_3$. In acidified soln. the sodium polymolybdate, which is first formed, gradually decomposes and yields a highly ionized polymolybdic acid, which causes the p_H of the soln. to assume slightly lower values than would be produced by the hydrochloric acid. A further addition of acid causes the ionization of the poly-acid to be thrown back until only non-ionized molybdenum trioxide remains in soln.; only from relatively conc. soln. is the trioxide precipitated on boiling. The changes of conductivity during the titration in general confirm the results obtained by the electrometric method. The addition of a weak acid, such as acetic or phenylacetic, to a sodium molybdate soln. causes the formation of a stable polymolybdate, $Na_2O.3MoO_3$, which is not further decomposed by the weak acid; in soln. containing monochloroacetic acid, the salt formed has a composition between $Na_2O.3MoO_3$ and $Na_2O.5MoO_3$. In soln. of molybdic acid there probably exists an equilibrium of the type $H_2[O(MoO_3)_n] \rightleftharpoons 2H^{\cdot}+[O(MoO_3)_n]''$, where n is about 4. Observations were also made by A. Travers and L. Malaprade, by A. Dumansky and co-workers, W. F. Jakob and W. Trzebiatowsky, and D. D. Peirce and L. F. Yntema.

J. Reich found that the olive-green liquid obtained by the electrolysis of a soln. of molybdenum trioxide in sulphuric acid—*vide supra*—has a potential of

—0·76 volt with smooth platinum, and —0·91 volt with platinized platinum against a mercurous sulphate electrode. A. Iléeff studied the thermoelectric force of powdered molybdenum trioxide compressed into pastilles. E. Wedekind and C. Horst found the **magnetic susceptibility** to be $0·876 \times 10^{-6}$ mass unit at 19·5°. S. Berkman and H. Zocher gave $0·12 \times 10^{-6}$ mass unit.

G. C. Gmelin[4] discussed the physiological action of salts of molybdic acid. T. G. y Arnal studied the reactions of molybdic acid with various salts of the metals. The ready reduction of molybdenum trioxide was discussed by W. Muthmann,[5] and O. F. von der Pfordten, and the formation of complex anions, by R. Abegg and G. Bodländer. Complex salts with the oxides of phosphorus, arsenic, antimony, bismuth, and other oxides have been prepared by O. W. Gibbs, etc. K. W. G. Kastner observed that when molybdenum trioxide is heated in **hydrogen,** it is reduced to the metal. E. W. Engle noticed that the reduction commences at about 300°; and M. Guichard added that it is reduced to MoO_2 between 300° and 470°, without forming intermediate oxides, and over 500°, it is reduced to the metal: $MoO_2 + 2H_2 \rightleftharpoons 2H_2O + Mo$—*vide supra.* F. R. M. Hitchcock noticed that in the reduction of molybdenum trioxide by hydrogen, a gas, probably impure nitrogen, is formed. The tendency to form a little nitride when one of the lower oxides molybdenum is heated in air has been observed by E. Uhrlaub. G. Canneri studied the reduction of molybdates with hydrogen. K. W. G. Kastner found that in the presence of hydrochloric acid and potassium amalgam, or zinc, or copper—or several other metals—molybdenum trioxide is reduced to a blue soln. of a salt of a lower oxide. C. Reichard also observed that in the presence of zinc and dil. hydrochloric or sulphuric acid, molybdenum trioxide gives a brown coloration which soon becomes pale green; and that molybdates give a transient reddish-brown coloration and then a greyish-brown precipitate. E. Wrede found molybdenum trioxide not so good as tungsten trioxide as a target for indicating the magnetic separation in a stream of unimolecular hydrogen. From the conductivity of flames charged with molybdenum trioxide, L. Rolla and G. Piccardi calculated the electronic affinity potential to be 2·73 volts. W. H. Rodebush and W. A. Nichols found that atomic **oxygen,** like atomic hydrogen, reduces the trioxide. For the action of **water,** *vide infra.* The aq. soln. has a sharp metallic taste, and reddens litmus, and, according to G. C. Wittstein, and A. Müller, it turns turmeric brown, especially in hydrochloric or nitric acid soln. For the action of **hydrogen dioxide,** *vide infra,* permolybdic acid. E. Spitalsky and A. Funck discussed the homogeneous catalytic decomposition of hydrogen dioxide by sodium molybdate. J. A. Hedvall and N. von Zweigbergh found that barium dioxide begins to react at about 200°—*vide* the molybdates.

H. Rose found that dry **chlorine** converts molybdenum trioxide into the dioxychloride less readily than is the case with the dioxide; H. E. Quantin, that at a dull red-heat, a mixture of chlorine and carbon monoxide forms molybdenum pentachloride. The attack by chlorine was studied by R. Wasmuth; and the attack by **chlorine trifluoride,** observed by O. Ruff, and H. Krug, proceeds with incandescence. H. Debray observed that **hydrogen chloride** at 150°–200°, forms the white dihydrochloride, $MoO_3.2HCl$; and K. W. G. Kastner, that boiling **hydrochloric acid** forms a blue soln. with the evolution of oxygen, and with boiling **hydriodic acid,** iodine separates and a green and then a blue soln. is formed. B. Kalischer found that when molybdenum trioxide is digested with alcoholic hydrochloric acid, a green soln. is obtained which does not yield a crystalline substance, but on evaporation, it furnishes a gelatinous, dark green mass which dissolves partially in water to form a brown soln. The original green soln. gives a double salt with pyridine hydrochloride. With alcoholic **hydrobromic acid,** no smell of aldehyde can be observed, and a yellowish soln. is obtained which behaves something like that obtained with the hydrochloric acid soln. Aqueous hydrobromic acid forms with molybdenum trioxide a deep brown soln. which becomes blue when water is added. No definite salt can be isolated from the soln., but if it be sat. with hydrogen bromide, it gives a brown, granular mass with pyridine hydrobromide. H. O. Schulze found that molybdenum trioxide decomposes **potassium iodide** especially in the presence of air, similarly also with the **alkali bromides and chlorides.** The reaction was also studied by C. F. Schönbein. W. R. E. Hodgkinson and F. K. S. Lowndes found that if a little molybdenum trioxide be added to molten **potassium chlorate,** oxygen and chlorine are evolved.

According to K. W. G. Kastner, a little **hydrogen sulphide** in the presence of water, or by the aid of heat, forms sulphur dioxide and sulphur, and sulphuric acid and a blue oxide. E. Uhrlaub observed that with an excess of hydrogen sulphide under similar conditions, molybdenum sulphide is formed. E. Abel studied the catalytic effect of the trioxide on the reaction between hydrogen dioxide and sodium thiosulphate. R. D. Hall observed that when heated with **sulphur monochloride,** the molybdenum oxide dissolves in the liquid and a volatile oxychloride is formed.

E. Uhrlaub found that when the trioxide is heated with **ammonia,** it is decomposed—*vide* nitrides, **8.** 49, 12 and 21. T. Curtius and F. Schrader said that **hydrazine hydrate** is vigorously decomposed forming molybdenum dioxide; and W. F. Jakob and W. Kozlowsky studied the reaction whereby quinquevalent molybdenum and nitrogen are formed. C. H. Ehrenfeld, and P. Sabatier and J. B. Senderens observed no reaction with **nitric oxide** at 500°. K. W. G. Kastner found that in the presence of water, and **nitrous acid,** the blue oxide is formed. R. Hac and V. Netuka studied the reduction of nitric acid to nitric oxide by ferrous chloride in an acidic soln. with molybdic acid as catalyst. P. Kulisch found that molybdenum trioxide is slowly attacked by **phosphine** in the cold and more rapidly when heated, a blue oxide being formed; C. H. Ehrenfeld said that purple Mo_2O_4 is formed. A. Michaelis observed that it is coloured blue by **phosphorus trichloride,** and in a sealed tube at 160°, it reacts: $MoO_3+PCl_3=MoO_2+POCl_3$; and with **phosphoryl chloride:** $2POCl_3+3MoO_3=3MoO_2Cl_2+P_2O_5$. H. Schiff found that with **phosphorus pentachloride,** molybdenum trioxide is coloured blue and then violet, heat is developed, and white and red vapours are given off—molybdenum oxychloride is formed. C. H. Ehrenfeld added that molybdenum pentachloride, mixed with some lower chlorides, is produced. According to J. J. Berzelius, with **phosphoric acid,** a lemon-yellow complex salt is formed—*vide infra*, the phosphomolybdic acids. When fused with **microcosmic salt,** molybdenum trioxide forms a colourless mass in the oxidizing flame, and in the inner flame a blue or grey mass. C. H. Ehrenfeld found that **arsine** acts like phosphine.

J. J. Berzelius observed that an aq. soln. of **boric acid** dissolves molybdenum trioxide; and fused **borax** dissolves molybdenum trioxide forming a clear glass in the oxidizing flame, but in a reducing flame, brown flecks of molybdenum dioxide are formed. K. W. G. Kastner observed that when the trioxide is heated with **carbon,** it is reduced to the metal. When the reduction is performed under definite conditions a factor can be obtained which represents the result with a known amount of molybdate, and, keeping rigorously to the same conditions, it can be assumed that the reduction proceeds to the same extent, and the factor can be employed to determine the amount of molybdenum in a given soln. H. Moissan, and H. N. Warren observed that with **calcium carbide,** a molybdenum-calcium alloy is formed. F. Göbel reduced molybdenum trioxide to a brown or violet-brown oxide by heating it in **carbon monoxide,** and W. Muthmann observed that the trioxide is successively reduced to $Mo_5O_{12}\rightarrow MoO_2\rightarrow$ and finally the metal. K. Chakravarty and J. C. Ghosh studied the catalytic action on the reaction between carbon monoxide and hydrogen. J. J. Berzelius observed that **carbon dioxide** does not unite with molybdenum trioxide. C. H. Ehrenfeld found that **ethylene** reduces the heated trioxide to bronze-coloured Mo_2O_5; similarly also with **acetylene,** but in addition a molybdenum carbide is formed; **methane** reduces the heated trioxide to the dioxide and the metal; **ethane** has no action.

J. Milbauer found that when the trioxide is fused with **potassium thiocyanate,** molybdenum disulphide, potassium thiomolybdate, and potassium cyanide are formed. A. Rosenheim and M. Koss obtained a deep red soln. by boiling an excess of molybdenum trioxide with a 10 per cent. aq. soln. of **thiocyanic acid.** On adding pyridine or quinoline, complex salts are deposited. G. A. Barbieri found that if an excess of **ammonium or potassium ferrocyanide,** followed by a large excess of an ammonium salt, is added to the soln. of a molybdate acidified with acetic acid, a lemon-yellow *precipitate*, $(NH_4)_4Fe(CN)_6.2MoO_3.3H_2O$, is obtained which is so sparingly soluble in conc. soln. of ammonium salts that the separation of molybdic acid is almost quantitative. H. E. Quantin passed the vapour of **carbon tetrachloride** over heated molybdenum trioxide, and obtained molybdenum oxychloride ; at a red-heat, molybdenum pentachloride is formed ; P. Camboulives added that this reaction occurs at 510°, but A. Michael and A. Murphy said at about 280°, and added that with a mixture of chlorine and carbon tetrachloride vapour at 200°, a yellowish-green oxychloride is formed, mixed with unchanged molybdenum trioxide ; at 225°, a mixture of MoO_2Cl_2 and $MoOCl_4$ is produced ; and at 240°, molybdenum pentachloride. According to A. Benrath, an aq. soln. of ammonium molybdate when diluted with an equal vol. of either ethyl **alcohol** or methyl alcohol and exposed to sunlight changes to blue after a short exposure, and a reddish-brown substance is deposited on the side of the flask on which the light falls. This compound has the formula $(NH_4)_2MoO_4.2MoO_3.2MoO_2.6H_2O$. In this formation only the complex acid group, MoO_3, and not the neutral ammonium molybdate, is reduced. Colloidal molybdic acid is rapidly reduced by alcohol to the blue oxide, Mo_3O_4 ; and S. Ghosh and A. K. Bhattacharya studied the photochemical reduction of molybdic acid by ethyl alcohol. L. Fernandes studied compounds of molybdenum trioxide with gallic acid, pyrocatechol, and pyrogallol ; E. Darmois, and T. S. Patterson and C. Buchanan, the effect of the sodium salt on the optical activity of **malic acid,** and tartaric acid. C. E. Guignet found molybdic acid to be a solvent for prussian blue. M. D. de Plaza studied the action of ammonium molybdate on potassium isobutylxanthate. H. N. Warren said that molybdenum trioxide is easily reduced when heated with **silicon.** L. Kahlenberg and W. J. Trautmann observed that a good reaction occurs when a mixture of molybdenum trioxide and silicon is heated in the electric arc furnace. G. Rauter found that when heated with **silicon tetrachloride,** chlorine, silica, $MoCl_5$, $MoOCl_4$, and MoO_2Cl_2, are formed ; C. H. Ehrenfeld observed no reaction when the two compounds are heated together. K. Fuwa studied the colouring action of molybdenum compounds on glass.

J. L. Gay Lussac and L. J. Thénard, and K. W. G. Kastner found that **potassium** or **sodium,** when heated with molybdenum trioxide, reduce it with incandescence to the metal. H. N. Warren found that when the trioxide is heated with molten **magnesium,** a violent detonation occurs ; and C. H. Ehrenfeld found that with powdered magnesium in air, the hemitrioxide is formed, and in hydrogen, the dioxide ; with **zinc,** in air, the hemipentoxide is formed ; and in hydrogen, Mo_4O_9 ; and with **aluminium,** the blue oxide is formed in air, and in hydrogen, no action occurs, probably because the trioxide is reduced by the hydrogen before the aluminium can act—*vide supra*, the preparation of molybdenum. It is generally supposed—W. A. Noyes and E. D. Frohman, D. L. Randall, C. Reinhardt, W. Scott, and B. Glassmann—that when a soln. of say ammonium molybdate is reduced by zinc and dil. sulphuric acid, out of contact with air, a salt of the oxide, Mo_2O_3, is formed, and volumetric methods for determining molybdenum, by the titration of the reduced oxide back to MoO_3, have been based on this assumption. It is, however, very difficult to drive the reduction until all the MoO_3 is reduced to Mo_2O_3. E. H. Miller and H. Frank, and A. A. Blair and J. E. Whitfield, said that an acid soln. of the trioxide is reduced by zinc to $Mo_{24}O_{37}$; O. F. von der Pfordten said Mo_5O_7 ; and A. Werncke, O. S. Doolittle and A. Eavenson, and C. Jones, $Mo_{12}O_{19}$, whilst C. B. Dudley obtained slightly different results. E. Berger and L. Delmas found that the presence of molybdenum trioxide facilitates the combustion of carbon in air. According to A. C. Chapman and H. D. Law, molybdenum trioxide is completely reduced to the molybdic oxide by the action of zinc or magnesium in sulphuric or hydrochloric acid soln.; zinc coated with nickel, silver, cadmium, or platinum also effects complete reduction; the action is fastest with zinc coated with cadmium. C. Boulanger studied the reduction of soln. of molybdenum salts by zinc, and aluminium. A. Chilesotti found that **mercury, tin,** and **lead** reduce a hydrochloric acid soln. of molybdenum trioxide to form molybdenum trichloride. G. Cannerei studied the reduction with tin. J. J. Berzelius said that **molybdenum** has no action when heated with the trioxide, but G. E. Uhrlaub observed that molybdenum reduces molybdenum trioxide suspended in water to a blue soln. K. Someya found that bismuth and lead amalgams reduce molybdates to quinquevalent molybdenum. According to M. Guichard, when a soln. of the compound $MoO_3.SO_3$, containing not less than 560 grms. H_2SO_4 per litre, is placed in contact with a large excess of powdered molybdenum in a closed vessel for a period of several months, a brown soln. is obtained which contains a salt of the oxide Mo_2O_5 and not of the oxide MoO_2 as stated by C. F. Rammelsberg. This fact, taken in conjunction with the results obtained by G. Bailhache, and P. Klason, renders it probable that the oxide MoO_2 does not form salts. G. E. Uhrlaub found that **stannous chloride** reduces molybdenum trioxide to a blue oxide; and E. D. Campbell said that the reduction of a hydrochloric acid soln. of the trioxide forms molybdenum pentachloride, which can be titrated back by a soln. of potassium dichromate. A. Geuther observed that the vapour of **ferric chloride** is absorbed by red-hot molybdenum trioxide to form ferric oxide and molybdenum oxychloride. According to R. H. Bradbury, an aq. soln. of **potassium chromate** reacts: $2K_2CrO_4+MoO_3=K_2Cr_2O_7+K_2MoO_4$; and with molten **potassium dichromate,** potassium chromatotrimolybdate is formed. The catalytic effect of molybdenum oxide in the oxidation of ammonia, and sulphur dioxide is discussed in connection with these compounds; C. Killing discussed the effect of molybdenum oxide in thoria gas mantles (*q.v.*). H. Brintzinger and F. Oschatz studied the electrometric titration of molybdates with **chromium dichloride,** following the reaction down to the formation of trivalent molybdenum. D. Balareff and N. Lukowa examined the effect of molybdenum trioxide on the boiling temp. of **calcium carbonate.**

According to T. Graham,[6] a soln. of sodium molybdate can be decomposed by the gradual addition of an excess of hydrochloric acid without an immediate precipitation of molybdenum trioxide. The acid liquor may gelatinize in a few hours on a dialyzer, but it again passes into the sol-form as the salts diffuse away. After repeated additions of hydrochloric acid, and a dialysis of several days, about 60 per cent. of the oxide remains as a **colloid solution of molybdic acid.** During the dialysis, endosmosis is great, so that the acid soln. in the dialyzer increases 2 or 3 times its original volume. The consequent dilution makes the purification slow. The colloidal soln. is yellow; it has an astringent taste, and is acidic to test-paper. It is fairly stable, and the acid can be dried at 100° without losing its solubility. The dry acid is more or less vitreous like gum or gelatin, and sometimes adheres so strongly to the surface of the evaporating basin as to detach portions of it. When heated short of its volatilizing temp., the powder all dissolves in a soln. of potassium carbonate or hydrocarbonate with the evolution of carbon dioxide. The colloid forms crystalline salts with the alkalies; and it becomes insoluble when heated for some time with hydrochloric acid or other strong acids. A. Sabanéeff, C. E. Linebarger, and A. Lottermoser obtained a similar product; and probably also F. Ullik—*vide infra.*

A. Sabanéeff found that when the dialyzed soln. is evaporated over sulphuric acid, in vacuo, it leaves transparent, hygroscopic, gum-like crusts, soluble in water without change, but on heating the soln. a white precipitate separates, and on evaporating to dryness an insoluble residue is left. Immediately after preparation, the salt contains 11·2 per cent. of water; after drying for several weeks over sulphuric acid, only 6·92 per cent. With the time of drying, the solubility of molybdic acid in water is found to decrease, and after some time it becomes insoluble. The depression of the f.p. for soln. containing 1·6–5·1 parts in 100 parts of water gives a mol. wt. of 608–631, the number calculated for $(MO_3)_4$ being 576. According to A. Rosenheim and I. Davidsohn, the soln. prepared by T. Graham's method probably contain no colloidal acid, since the addition of electrolytes does not cause precipitation. Colloidal molybdic acid was obtained by evaporating a soln. of the dihydrate over sulphuric acid, under reduced press., at 20°, or by warming a soln. of a mol of sodium molybdate and 4 mols of hydrochloric acid. The vitreous mass so obtained is readily soluble, forming an opalescent liquid, from which electrolytes readily precipitate the colloidal acid. A. V. Dumansky and co-workers found that the conductivity curve, and the curve for the lowering of the f.p. on adding acid to a soln. of sodium molybdate, show well-defined maxima and minima corresponding with the formation of intermediate complexes before colloidal particles of molybdic acid are formed, say $Na_2MoO_4+2HCl=2NaCl+H_2MoO_4$, and $H_2MoO_4+MoO_4''=H_2O+[MoO_4.MoO_3]''$. When small proportions of hydrochloric acid are successively added to a soln. of sodium molybdate, the free acid acts in successive stages: $Na_2MoO_4+H_2MoO_4=Na_2O(MoO_3)_2+H_2O$, etc.; this is indicated by the electrolytic and cryoscopic methods. The two salts, $Na_2O(MoO_3)_4$ and $Na_2O(MoO_3)_8$, were synthesized. The colloidal particles appear only when the octomolybdate is formed. The colloid was not coagulated either by cooling or heating or addition of electrolytes, and had an apparent mol. wt. of 1139; it thus could be classed with the semi-colloids. A second modification of the colloid—a suspension of the oxide MoO_3, which has much larger particles, exhibiting Brownian movement—also exists. G. Wegelin prepared colloidal soln. by a prolonged grinding of the powder in an agate mortar.

G. Bruni and N. Pappada observed no variation in the vap. press. of colloidal soln. They applied the term semi-colloid to colloidal molybdic acid prepared by T. Graham's process, because it readily passes through a dialyzer, and gives small depressions of the f.p. which are quite appreciable, and proportional to the concentration. True colloids do not really dissolve, but they remain suspended in the liquid in a fine state of subdivision, and they have a constant f.p. On freezing true solutions there are three co-existent phases—ice, soln., and vapour—the system is mono-variant; whilst in the case of a soln. containing a solid in suspension, there is another phase and the system is non-variant. L. Wöhler and W. Engels confirmed G. Bruni and N. Pappada's observation that with a 3 weeks' dialysis of T. Graham's soln., all the molybdic acid diffuses through the parchment. H. Picton and S. E. Linder also found that T. Graham's colloidal soln. does not show Tyndall's effect. The ultramicroscopic observations of L. Wöhler and W. Engels show that soln. of molybdic acid can be obtained in the colloidal or non-colloidal state. By acidifying a soln. of a molybdate, the molybdic acid polymerizes but the particles are so small that the soln. behaves as an electrolyte in diffusing through a parchment membrane; whether or not the particles coalesce further depends on the age of the soln., the presence of electrolytes, the temp. and other physical conditions. W. von Behren and I. Traube studied the colloid →crystal transformation. S. Ghosh and N. R. Dhar, and D. N. Chakravarti and N. R. Dhar measured the viscosity of colloidal soln. of molybdic acid. R. Wintgen found that the sp. gr. and refractive index of the colloidal soln. are linear functions of the conc.; and the sp. vol., v, and the product of the sp. vol. and the refractive index, μ, are linear functions of the percentage content, p, of the disperse phase so that $v=1{\cdot}00289-0{\cdot}0079682p$, and $v\mu=1{\cdot}33630-0{\cdot}008403p$. W. Reinders discussed the distribution of the colloid between two liquids; and E. F. Krause and A. V. Novoseloff, the adsorption of the colloid by the membrane in ultrafiltration.

C. F. Bucholz [7] found that 100 parts of cold water dissolve 0·2 part of molybdenum trioxide; and H. Debray, 0·18 part of cold water and less in hot water; and C. Hatchett said that 100 parts of hot water dissolve 0·104 part of the trioxide.

The **soluble molybdic acid** of F. Ullik is probably identical with T. Graham's **colloidal molybdic acid.** F. Ullik prepared it by treating a thin mush of barium molybdate with enough sulphuric acid to precipitate the barium as sulphate. The filtrate is treated with barium chloride and hydrochloric acid, and again with sulphuric acid. The colourless soln., when evaporated over sulphuric acid, dries to an amorphous powder. This is soluble in water when freshly prepared, but with ageing it becomes insoluble. If the soln. be evaporated on a water-bath, and dried at 100°, or if magnesium molybdate be treated with an excess of nitric acid, and the washed powder dried at 100°, the composition of the product approximates $MoO_3.nH_2O$, where n lies between 0·20 and 0·22. L. S. Bhatia and co-workers, and W. V. Bhagwat and N. R. Dhar studied the coagulation of colloidal molybdic acid. E. F. Krauze and A. V. Novoseloff considered that the adsorption of molybdic acid by porous clay tubes covered with collodion is a mechanical process in which large aggregates are held in the pores. The adsorption is preceded by a process of complex formation.

J. J. Berzelius obtained small, silky, crystalline scales by the spontaneous evaporation of a soln. of molybdenum or one of its lower oxides in an excess of nitric acid. The product lost on ignition about 2 per cent. of water. The existence of two definite hydrates has been established. G. F. Hüttig and B. Kurre measured the dissociation temp. of the hydrates, starting from the yellow precipitate from a nitric acid soln. of ammonium molybdate. The results, plotted in Fig. 12, show that these two hydrates exist as chemical individuals. The white α-monohydrate differs from the yellow dihydrate, even in aq. soln. A. Mazzucchelli and M. Borghi showed that the α-monohydrate is readily obtained by treating methyl molybdate with water. Its behaviour with tartaric acid and hydrogen dioxide is analogous to that of the yellow acid, but the rotary powers of soln. of the same composition are different, and the maximum corresponds with the existence of a compound $C_4H_4O_6.5(MoO_3.H_2O_2)$, thus affording a further proof of the difference between the two acids.

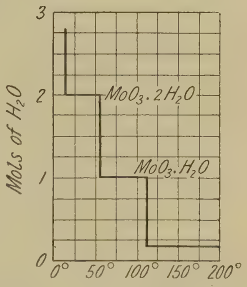


FIG. 12.—Dissociation Temperatures of the Hydrates of Molybdenum Trioxide.

The *monohydrate* of molybdic oxide, $MoO_3.H_2O$, is considered to be a kind of **metamolybdic acid,** H_2MoO_4, because the X-radiograms of H. C. Burger show that the angles of reflection are different from those of molybdenum trioxide. F. Ullik prepared this hydrate by treating a mol of magnesium molybdate with 2 mols of nitric acid, and allowing the white powder to stand for some time when prismatic crystals are formed. L. C. A. Vivier found that white crystals of this hydrate separated from a soln. of ammonium molybdate in nitric acid, and from a soln. of an ordinary molybdate on standing for several days at 50° to 60°. F. Ephraim and M. Brand obtained the monohydrate as a precipitate on mixing a soln. of a mol of normal lithium molybdate with 7 mols of nitric acid of sp. gr. 1·20, while warmed on a water-bath. A. Rosenheim and A. Bertheim obtained it by warming the dihydrate to 70°. A. Rosenheim and I. Davidsohn designate this the *β-monohydrate* to distinguish it from the *α-monohydrate* which is formed in asbestos-like, white needles when a soln. of the dihydrate is kept at 40°–50°. The β-form occurs in small white needles. The α-form differs from the β-hydrate in having a more definite crystal habit, and in the rapidity with which it settles from a suspension in water. The α-hydrate is also said to lose its water of crystallization more readily than the β-form. L. C. A. Vivier said that the monohydrate forms crystals which are probably hexagonal. A. Rosenheim and I. Davidsohn found the solubility of the α-monohydrate, S grms. MoO_3 per 100 grms. of water:

	14·8°	24·6°	36·8°	45·0°	52·0°	60·0°	70·0°	80·0°
S . .	0·2117	0·2619	0·3085	0·3661	0·4184	0·4685	0·4231	0·5212

At about 60°, there is a break in the curve, indicating that the α-monohydrate is transformed into the β-variety. The mol. conductivity, μ mhos, of the soln. of the α-monohydrate closely resembles that of methyl molybdate. For soln. with a mol of the α-monohydrate in v litres, at 25°,

v . .	31·3	62·6	125·2	250·4	500·8	1001·7
μ . .	71·4	89·4	95·2	96·9	100·3	104·1

Cryoscopic determinations show that the molybdic acid in the α-monohydrate has a smaller mol. wt. than is the case with the dihydrate. The rate of hydrolysis of methyl molybdate shows that the α-monohydrate is a weaker acid than the dihydrate.

According to A. Travers and L. Malaprade, cold, aq. soln. of the mono- or di-hydrate of molybdenum trioxide differ from soln. made at 100° and cooled, both in colour, and in their reactions with potassium ferrocyanide. It is assumed that both molybdic acid, $H_2[MoO_4]$, and tetramolybdic acid, $H_2[4MoO_3.O]$, are present in the soln., and that the latter ionizes: $H_2O.4MoO_3 \rightleftharpoons 2H^{\cdot}+[4MoO_3.O]$. This is confirmed by the neutralization curve which shows inflexions at $4MoO_3.K_2O$ and $MoO_3.K_2O$, the first resulting from the complete neutralization of the acid $4MoO_3.H_2O$, and the second from the decomposition of the salt formed first by the alkali. In support of this, the reactions of the tetramolybdate are found to be quite different from those of the neutral salt. From the analogy with the tungstic acids, $4MoO_3.H_2O$ is called metamolybdic acid. S. I. Diatschkovsky and A. V. Dumansky showed that with soln. of 10 eq. of sodium molybdate and 10 eq. of hydrochloric acid, the complex tetramolybdate, $Na_2O(MoO_3)_4$, was formed; with 12 eq. of acid, $Na_2O(MoO_3)_8$ was produced. This soln. does not coagulate at 100° nor when electrolytes are added.

M. Jungck, and S. Kern made some observations on the yellowish crystalline substance which separates when a soln. of an alkali molybdate in nitric acid is allowed to stand for a time. F. Parmentier showed that the deposit is the *dihydrate* of molybdic acid, $MoO_3.2H_2O$, or, if H_6MoO_6 be orthomolybdic acid, it can be regarded as **paramolybdic acid,** H_4MoO_5, although the term para-molybdate is usually applied to a salt of another molybdic acid. The dihydrate is not formed in hydrochloric acid soln. of the alkali molybdates. J. H. Graham, and A. A. Blair and J. E. Whitfield also found that the yellow deposit from the nitric acid soln. of alkali molybdate is dihydrated molybdenum trioxide. J. Terwelp obtained the dihydrate in the anode chamber during the electrolysis of soln. of molybdates. A. Rosenheim obtained it by pouring a soln. of 15 grms. of commercial (3 : 7)-ammonium molybdate in a litre of water with constant stirring to 29–30 per cent. nitric acid (300 c.c. of nitric acid of sp. gr. 1·42 diluted to a litre), and allowing the soln. to stand at 20°-25° for 8 to 10 days after inoculation with a crystal of the dihydrate. F. Parmentier, and L. C. A. Vivier observed that the lemon-yellow, prismatic crystals are monoclinic; and A. de Schulten added that the axial ratios are $a : b : c : =1·0950 : 1 : 1·0664$, and $\beta=90° 41'$. The angle between the basal plane and the orthopinacoid, *i.e.* (001) : (100), is 89° 19′, making the crystals appear at first glance as though they were cubes. The sp. gr. is 3·124 at 15°. F. Parmentier said that the crystals are efflorescent and lose half their water over sulphuric acid, in vacuo; and at 200°, they lose all their water. A. Rosenheim and A. Bertheim found that the dihydrate cannot be regenerated after it has been converted at 70° into the monohydrate.

E. Bruchhaus examined the reduction of ammonium molybdate by hydrogen. The solubility, S grms. of MoO_3 in 100 grms. of water, is,

	18°	23°	40°	50·2°	60°	70°	75°	79°
S .	0·1066	0·1856	0·4761	0·6873	1·2057	2·0550	2·0920	2·1064

There is a marked break in the solubility curve at 70° corresponding with the transformation of the dihydrate into the monohydrate. A. Rosenheim and

I. Davidsohn found that the solubility curves of the dihydrate and the α-monohydrate intersect at 32°; and A. Rosenheim and A. Bertheim showed that there is a change in the direction of the solubility curve of the dihydrate at 50°, and possibly below 18° another change of direction occurs. The solubility determined by saturating at a particular temp. is lower than that obtained by saturating at a higher temp. and then cooling in contact with solid. This anomalous behaviour seems not to be due to the formation of a colloidal soln., because the apparently supersaturated soln. diffuses quite readily. The cryoscopic observations of A. Rosenheim and A. Bertheim showed that the mol. wt. approximates $(MoO_3)_4$; and those of A. Mazzucchelli and G. Zangrilli, $(MoO_3)_6$. The solubility of the dihydrate is greatly increased by the addition of ammonium salts; *e.g.* with a 10 per cent. soln. of ammonium hydrosulphate, the solubility, S grms. of MoO_3 per 100 grms. of solvent, is 1·927 at 29·6°; 2·753 at 31·5°; 3·436 at 41·8°; and 3·769 at 49·7°. This is taken to mean that the dihydrate is not a colloid. The mol. conductivity, μ mhos, of soln. with a mol of the dihydrate in v litres of water, at 25°, is,

v	16·56	33·12	66·24	132·48	264·96	529·92	1059·84
μ	98·28	130·10	150·0	159·7	163·5	168·7	180·3

Acetic acid and boric acid exert scarcely any influence on the conductivity of molybdic acid soln. Tartaric acid, malic acid, and mannitol greatly increase the conductivity, and this is attributed to the formation of a complex molecule. On account of hydrolysis of the complex molecule at high dilution, the increase of the conductivity diminishes somewhat with the dilution. Oxalic acid and iodic acid, which form complex molecules with molybdic acid, which can be isolated, diminish the conductivity, but this may be due to the complex ion having a smaller speed of migration. Phosphoric acid also increases the conductivity, the maximum being reached when phosphodecamolybdic acid is present. The ionization constant of the acid in soln. of the dihydrate was found by A. Rosenheim and A. Bertheim to be $k=0{\cdot}052$ at 25° when calculated from the velocity of hydrolysis of methyl acetate which is 0·88. These results all show that the acid is greatly ionized in aq. soln. Cryoscopic measurements indicate that in the soln., an octomolybdic acid, $H_2Mo_8O_{25}$, is present, and these are supported by the fact that on adding ammonium salts, ammonium octomolybdate, $(NH_4)_2Mo_8O_{25}.13H_2O$, separates. E. Darmois and A. Honnelaitre, and A. Honnelaitre made a study of complexes of molybdic and malic acids; and E. Rimbach and P. Ley, mixtures of molybdic and hydroxy-organic compounds which were found to augment the acidity of molybdic and boric acids. R. F. Weinland and co-workers also studied this subject. F. Parmentier observed that the dihydrate is sparingly soluble in water and acids at different temp.; it dissolves completely in soln. of alkali hydroxides and carbonates, and, on evaporation, these soln. furnish ordinary molybdates. K. von der Heide studied the action of hydroxylamine, and of potassium cyanide. The soln. in aq. ammonia remains clear when magnesia mixture is added, and precipitates molybdenum trioxide when nitric acid is added to the aq. soln. E. Müller, H. H. Willard and F. Fenwick, and O. Tomicek studied the electrometric reduction of soln. of sexivalent molybdenum by titanous salt soln. R. Hac and V. Netuka studied its catalytic action on the reduction of nitric acid by ferrous chloride.

According to F. Mylius, no solid **orthomolybdic acid,** H_6MoO_6, exists corresponding with orthotelluric acid, H_6TeO_6. The colourless molybdic acid obtained in aq. soln. corresponds with *allo*telluric acid, with which it agrees in having an indefinitely large solubility in cold water, complex composition, in being soluble in alcohol, in being precipitated in the form of acid salts, and in precipitating solutions of proteids. Of the solid forms of molybdic acid, the yellow acid, H_3MoO_5, has the greatest solubility in water, and is slowly formed when soln. of molybdates or molybdic acid are treated with nitric or hydrochloric acid. As indicated above, the dihydrate, H_4MoO_5, is considered by A. Rosenheim and A. Bertheim to be an

octomolybdic acid, $H_2Mo_8O_{25}$, and it is assumed that in passing from one hydrated form to another, various complex intermediate polymerides of molybdic acid are formed—*vide infra.*

G. Jander and co-workers studied the complex acids, and some of the results have been summarized in connection with the electrometric titration of the acid. He gives for the condensation products :

$3[MoO_4{}'']+2H^{\cdot}=[Mo_3O_{11}{}'''']+H_2O$ stable in the region $p_H=6{\cdot}1$; $[Mo_3O_{11}{}'''']+H^{\cdot}=[H(Mo_3O_{11})''']$, called, by F. Ullik, the " dimolybdate " ; $2[H(Mo_3O_{11})''']+H^{\cdot}=[H(Mo_6O_{21})''''']+H_2O$, stable in the region $p_H=4{\cdot}5$, and called, by F. Ullik, " paramolybdates " ; $[H(Mo_6O_{21})''''']+H^{\cdot}=[H_2(Mo_6O_{21})'''']$, called, by F. Ullik, the " trimolybdates " ; $[H_2(Mo_6O_{21})'''']+H^{\cdot}=[H_3(Mo_6O_{21})''']$, stable with p_H approximately $2{\cdot}9$, and called, by F. Ullik, " tetramolybdates " or " metamolybdates " ; $2[H_3(Mo_6O_{21})''']+3H^{\cdot}=2[H_7(Mo_{12}O_{41})''']+H_2O$, called, by F. Ullik, " octomolybdates " ; $2[H_7(Mo_{12}O_{41})''']+H^{\cdot}=[H_7(Mo_{24}O_{78})''''']+4H_2O$, called, by F. Ullik, " decamolybdates " ; $[H_7(Mo_{24}O_{78})''''']+2H^{\cdot}=[H_9(Mo_{24}O_{78})''']$, called, by F. Ullik, " hexadecamolybdates " ; and $[H_9(Mo_{24}O_{78})'''+3H^{\cdot}=H_{12}(Mo_{24}O_{78})$, where p_H approximates $0{\cdot}9$.

REFERENCES.

[1] D. L. G. Karsten, *Mineralogische Tabellen,* Berlin, 54, 79, 1800 ; 70, 1808 ; J. F. L. Hausmann, *Handbuch der Mineralogie,* Göttingen, 336, 1813 ; 207, 1847 ; R. P. Greg and W. G. Lettsom, *Manual of the Mineralogy of Great Britain and Ireland,* London, 348, 1858 ; M. F. Heddle, *The Mineralogy of Scotland,* Edinburgh, **2.** 196, 1901 ; C. C. von Leonhard, *Handbuch einer topographischen Mineralogie,* Frankfort, 396, 1843 ; J. D. Dana, *A System of Mineralogy,* New York, 202, 1892 ; G. H. F. Ulrich, *Contributions to the Mineralogy of Victoria,* Melbourne, 7, 1870 ; W. P. Jervis, *Il tesori sotteranei dell' Italia,* Turin, **3.** 472, 1881 ; A. Breithaupt, *Berg. Hütt. Ztg.,* **17.** 125 1858 ; D. Lovisato, *Atti Accad. Lincei,* (4), **2.** 254, 1886 ; V. von Zepharovich, *Mineralogische Lexicon für das Kaiserthum Oesterreich,* Wien, 211, 1859 ; A. Frenzel, *Mineralogisches Lexicon für das Königreich Sachsen,* Leipzig, 208, 1874 ; G. A. Kenngott, *Die Minerale der Schweiz nach ihren Eigenschaften und Fundorten,* Leipzig, 366, 1866 ; P. Groth, *Die Mineraliensammlung der Universität Strassburg,* Strassburg, 113, 1878 ; G. C. Hoffmann, *Ann. Rep. Canada Geol. Sur.,* **9.** 17, 1898 ; *Annotated List of Minerals occurring in Canada,* Ottawa, 92, 1890 ; *Trans. Roy. Soc. Canada,* **7.** 65, 1890 ; C. F. de Landero, *Sinopsis mineralogica ó catalogo descriptivo de los minerales,* Mexico, 340, 1888 ; W. von Hisinger, *Samling till en mineralogisk geografi öfver Sverige,* Stockholm, 1808 ; A. des Cloizeaux, *Nouvelles recherches sur les propriétés optiques des cristaux,* Paris, 26, 1867 ; D. D. Owen, *Proc. Acad. Philadelphia,* **6.** 108, 1852 ; *Amer. Journ. Science,* (2), **14.** 279, 1852 ; W. E. Hidden and J. B. Mackintosh, *ib.,* (3), **38.** 485, 1889 ; T. S. Hunt, *ib.,* (2), **19.** 429, 1855 ; F. A. Genth, *ib.,* (2), **19.** 376, 1855 ; (2), **28.** 248, 1859 ; *The Minerals of North Carolina,* Washington, 40, 1891 ; A. Lacroix, *Minéralogie de la France et de ses colonies,* Paris, **3.** 8, 1901 ; E. Stöhr, *Die Kupfererze am der Mürtschenalp und der auf ihnen geführte Bergbau,* Zürich, 19, 1865 ; *Denks. Schweiz. Ges.,* **21.** 5, 1865 ; C. F. A. Tenne and S. Calderon, *Die Mineralfundstatten der Iberischen Halbinsel,* 116, 1902 ; W. F. Petterd, *Catalogue of the Minerals of Tasmania,* Launceston, 61, 1896 ; J. J. Berzelius, *Schweigger's Journ.,* **22.** 51, 1817 ; *Pogg. Ann.,* **4.** 153, 1825 ; **6.** 331, 369, 1826 ; **7.** 261, 1826 ; *Ann. Chim. Phys.,* (2), **17.** 5, 1821 ; F. von Kobell, *Charakteristik der Mineralien,* Nürnberg, 1831 ; *Geschichte der Mineralien,* München, 543, 1864 ; A. Raimondi, *Minéraux du Pérou,* Paris, 183, 1878 ; I. Domeyko, *Elementos de mineralojia,* Santiago, 87, 1879 ; A. E. Nordenskjöld, *Oefvers. Akad. Förh.,* **17.** 300, 1860 ; *Pogg. Ann.,* **112.** 160, 1861 ; W. T. Schaller, *Zeit. Kryst.,* **44.** 9, 1907 ; *Amer. Journ. Science,* (4), **23.** 297, 1907 ; F. N. Guild, *ib.,* (4), **23.** 455, 1907 ; P. P. Pilipenko, *Vernadsky's Festschrift,* Moscow, 189, 1914.

[2] H. V. Regnault, *Ann. Chim. Phys.,* (2), **62.** 356, 1836 ; R. Stierlin, *Journ. prakt. Chem.,* (2), **14.** 464, 1876 ; H. Debray, *Compt. Rend.,* **46.** 1098, 1858 ; M. Liebert, *Beiträge zur Kenntniss der sogenannten Vanadinmolybdänsaure,* Halle, 1891 ; L. Wöhler and W. Engels, *Koll. Beihefte,* **1.** 454, 1910 : P. Klason, *Ber.,* **34.** 153, 1901 ; W. Muthmann, *Liebig's Ann.,* **238.** 117, 1887 ; *Ber.,* **20.** 989, 1887 ; *Ueber niedere Oxyde des Molybdäns,* München, 1886 ; L. Rolla and G. Piccardi, *Atti Accad. Lincei,* (6), **5.** 546, 1927 ; J. J. Berzelius, *Svenska Akad. Handl.,* 145, 1825 ; *Pogg. Ann.,* **4.** 153, 1825 ; **6.** 331, 369, 1826 ; **7.** 261, **1826** ; *Ann. Chim. Phys.,* (2), **17.** 5, 1821 ; *Schweigger's Journ.,* **22.** 51, 1817 ; **47.** 87, 1826 ; *Ann. Phil.,* **11.** 235, 1826 ; *Edin. Journ. Science,* **4.** 133, 1826 ; C. W. Scheele, *Svenska Akad. Handl.,* **39.** 247, 1778 ; **40.** 238, 1779 ; L. Ott, *Elektrolyse geschmolzener Molybdate und Vanadate,* München, 23, 1911 ; F. Elias, *Beiträge zur Kenntnis der gelben Phospormolybdate,* Bern, 43, **1906** ; G. C. Wittstein, *Reperth. Pharm.,* **73.** 155, 1841 ; A. Arnfeld, *Beiträge zur Kenntnis der Phosphormolybdate,* Berlin, 19, 1898 ; W. D. Collins, H. V. Larr, J. Rosin, G. C. Spencer, and E. Withers, *Journ. Ind. Eng. Chem.,* **19.** 1369, 1927 ; J. von Liebig, *Kastner's Arch.,* **2.** 57, 1824.

[3] A. E. Nordenskjöld, *Oefvers, Akad. Förh.,* **17.** 300, 1860 ; *Pogg. Ann.,* **112.** 160, 1861 ; A. Safarik, *Sitzber. Akad. Wien,* **47.** 256, 1863 ; J. M. Eder, *ib.,* **92.** 340, 1885 ; *Monatsh.,* **6.** 495, 1885 ; R. Stierlin, *Journ. prakt. Chem.,* (2), **14.** 464, 1876 ; D. Balareff, *ib.,* **102.** 283, 1921 ;

A. Miolati, *ib.*, (2), **77**. 417, 1908 ; V. Eggertz, *ib.*, (1), **79**. 498, 1860 ; G. Merz, *ib.*, (1), **80**. 495, 1860 ; *Chem. News*, **3**. 146, 1861 ; A. Dumansky, A. P. Buntin, S. J. Dijatschowsky and A. G. Kniga, *Koll. Zeit.*, **38**. 208, 1926 ; A. Travers and L. Malaprade, *Bull. Soc. Chim.*, (4), **39**. 1406, 1543, 1926 ; H. T. Meyer, *Naturwiss.*, **18**. 34, 1930 ; W. F. Jakob and W. Trzebiatowsky, *Rocz. Chem.*, **9**. 676, 1929 ; K. W. G. Kastner, *Kastner's Arch.*, **26**. 465, 1835 ; A. A. Read, *Journ. Chem. Soc.*, **65**. 313, 1894 ; T. Carnelley, *ib.*, **33**. 273, 1878 ; E. Groschuff, *Zeit. anorg. Chem.*, **58**. 113, 1908 ; F. Hoermann, *ib.*, **177**. 145, 1928 ; W. G. Mixter, *Amer. Journ. Science*, (4), **29**. 488, 1910 ; D. Gernez, *Compt. Rend.*, **104**. 783, 1887 ; J. Férée, *ib.*, **122**. 733, 1896 ; G. A. Dima, *ib.*, **157**. 590, 1913 ; L. Bleekrode, *Proc. Roy. Soc.*, **25**. 322, 1877 ; *Phil. Mag.*, (5), **5**. 375, 439, 1878 ; E. L. Nichols and B. W. Snow, *ib.*, (5), **32**. 401, 1891 ; A. Iléeff, *Journ. Russ. Phys. Chem. Soc.*, **40**. 220, 1908 ; H. Buff, *Liebig's Ann.*, **103**. 883, 1857 ; **110**. 264, 1859 ; W. Jungck, *Zeit. anal. Chem.*, **15**. 290, 1876 ; T. de Grotthus, *Ann. Chim. Phys.*, (1), **58**. 10, 1806 ; *Phil. Mag.*, **25**. 330, 1806 ; T. Bergman, *Sciagraphia*, Leipzig, 93, 1782 ; M. Guichard, *Ann. Chim. Phys.*, (7), **23**. 498, 1901 , E. Wrede, *Zeit. Physik*, **41**. 569, 1927 ; P. Groth, *Chemische Krystallographie*, Leipzig, **2**. 110, 1908 ; R. E. Myers, *Journ. Amer. Chem. Soc.*, **26**. 1124, 1904 ; J. E. Moose and S. W. Parr, *ib.*, **46**. 2656, 1924 ; G. Gore, *Journ. Chem. Soc.*, **22**. 368, 1869 ; *Quart. Journ. Science*, **6**. 319, 1869 ; *Phil. Trans.*, **159**. 173, 1869 ; *Proc. Roy. Soc.*, **17**. 256, 1869 ; *Phil. Mag.*, (4), **37**. 470, 1869 ; *Electrochemistry*, London, 99, 1906 ; A. Chilesotti, *Atti Accad. Lincei*, (5), **12**. ii, 22, 67, 1903 ; *Zeit. Elektrochem.*, **12**. 143, 154, 173, 197, 1906 ; *Gazz. Chim. Ital.*, **33**. ii, 349, 1903 ; A. Chilesotti and A. Rozzi, *ib.*, **35**. i, 228, 1905 ; T. L. Phipson, *Chem. News*, **30**. 33, 1874 ; L. Schicht, *ib.*, **41**. 280, 1880 ; **42**. 331, 1880 ; **47**. 209, 1883 ; *Zeit. anal. Chem.*, **22**. 485, 1883 ; *Berg. Hütt. Ztg.*, **39**. 121, 1880 ; A. Breithaupt, *ib.*, **17**. 125, 1858 ; J. Terwelp, *Beiträge zur Elektrochemie der Molybdate*, Berlin, 23, 1903 ; A. Lacroix, *Mineralogie de la France et de ses colonies*, Paris, **3**. 8, 1901 ; J. Reich, *Elektrolytische Reduktion von Nitrokörpern mit Molybdän als Wasserstoffübertrager*, München, 1910 ; E. Wedekind and C. Horst, *Ber.*, **48**. 105, 1915 ; A. des Cloizeaux, *Nouvelles recherches sur les propriétés optiques des cristaux*, Paris, 26, 1867 ; L. Ott, *Elektrolyse geschmolzener Molybdate und Vanadate*, München, 23, 1911 ; E. Beckmann, *Zeit. phys. Chem.*, **53**. 129, 1905 ; C. F. Bucholz, *Scherer's Journ.*, **9**. 485, 1802 ; *Gehlen's Journ.*, **4**. 598, 1805 ; *Phil. Mag.*, **16**. 193, 1803 ; C. del Fresno, *Anal. Fis. Quim*, **24**. 707, 1926 ; *Zeit. Elektrochem.*, **36**. 163, 1930 ; J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1818 ; **23**. 186, 1918 ; *Lehrbuch der Chemie*, Dresden, **2**. 353, 1844 ; **3**. 1208, 1845 ; *Pogg. Ann.*, **8**. 23, 1826 ; J. B. A. Dumas, *Ann. Chim. Phys.*, (3), **55**. 129, 142, 1859 ; *Compt. Rend.*, **45**. 709, 1857 ; H. Debray, *Compt. Rend.*, **66**. 732, 1868 ; C. F. Rammelsberg, *Sitzber. Akad. Berlin*, 574, 1877 ; *Ber.*, **10**. 1776, 1877 ; A. Vandenberghe, *Mem. Cour. Acad. Belg.*, (4), **56**. 5, 1898 ; *Zeit. anorg. Chem.*, **10**. 47, 1895 ; **11**. 385, 397 1896 ; C. Zenghelis, *Zeit. phys. Chem.*, **50**. 219, 1904 ; K. Seubert and W. Pollard, *Zeit. anorg. Chem.*, **8**. 434, 1895 ; E. Friederich, *Zeit. Physik*, **31**. 813, 1925 ; J. H. Müller, *Journ. Amer. Chem. Soc.*, **37**. 2046, 1915 ; C. F. Plattner, *Die Probirkunst mit dem Löthrohre*, Leipzig, 1835 ; F. Beijerinck, *Neues Jahrb. Min. B.B.*, **11**. 442, 1897 ; L. G. Kollock and E. F. Smith, *ib.*, **23**. 669, 1901 ; *Zeit. Elektrochem.*, **7**. 957, 1901 ; E. F. Smith, *Amer. Chem. Journ.*, **7**. 329, 1885 ; E. F. Smith and W. S. Hoskinson, *ib.*, **7**. 90, 1885 ; P. H. M. P. Brinton and A. E. Stoppel, *Journ. Amer. Chem. Soc.*, **46**. 2454, 1924 ; H. T. S. Britton and W. L. German, *Journ. Chem. Soc.*, 2154, 1930 ; J. G. Gahn, *Gilbert's Ann.*, **14**. 235, 1803 ; W. D. Bancroft and H. B. Weiser, *Journ. Phys. Chem.*, **18**. 263, 1914 ; W. Lederer, *Darstellung und Untersuchung reinen, geschmolzen Molybdäns*, Erlangen, 14, 1911 ; S. M. Delépine, *Bull. Soc. Chim.*, (3), **29**. 1166, 1903 ; S. Berkman and H. Zocher, *Zeit. phys. Chem.*, **124**. 318, 1926 ; A. Berkenheim, *ib.*, **135**. 231, 1928 ; C. N. Riiber and J. Minsaas, *Ber.*, **59**. B, 2266, 1926 ; L. W. Andrews, *Proc. Iowa Acad.*, **32**. 267, 1925 ; T. W. Case, *Phys. Rev.*, (2), **9**. 305, 1917 ; J. O. Perrine, *ib.*, (2), **22**. 48, 1923 ; W. R. Mott, *Trans. Amer. Electrochem. Soc.*, **34**. 255, 1918 ; H. C. Germs, *Die thermische Analyse van Loodsulfaat, -Chromaat, -Molybdaat en -Wolframaat en van hun Binaire Combinaties*, Groningen, 1917 ; F. M. Jäger and H. C. Germs, *Zeit. anorg. Chem.*, **119**. 125, 1921 ; W. O. Collins, H. V. Farr, J. Rosin, G. C. Spencer and E. Wichers, *Journ. Ind. Eng. Chem.*, **19**. 1369, 1927 ; R. Robl, *Zeit. angew. Chem.*, **39**. 608, 1926 ; F. Förster and E. Fricke, *ib.*, **36**. 458, 1923 ; F. Förster, E. Fricke and R. Hausswald, *Zeit. phys. Chem.*, **146**. 81, 177, 1930 ; J. Maydel, *Zeit. anorg. Chem.*, **186**. 289, 1930 ; W. Biltz, *ib.*, **193**. 321, 1930 ; H. E. Buckley, *Zeit. Kryst.*, **75**. 26, 1930 ; P. Niggli, *ib.*, **75**. 254, 1930 ; J. Ewles, *Proc. Leeds Phil. Lit. Soc.*, **1**. 6, 1925 ; E. Péchard, *Compt. Rend.*, **112**. 720, 1891 ; **114**. 1481, 1892 ; E. Tiede and A. Schleede, *Naturwiss.*, **11**. 765, 1923 ; L. Rolla and G. Piccardi, *Atti Acad. Lincei*, (6), **5**. 546, 1927 ; H. Nisi, *Japan. Journ. Phys.*, **5**. 119, 1929.

[4] G. C. Gmelin, *Schweigger's Journ.*, **43**. 110, 1825 ; *Edin. Med. Journ.*, **3**. 324, 1827 ; T. G. y Arnal, *Anal. Soc. Fis. Quim.*, **26**. 435, 1928.

[5] O. W. Gibbs, *Amer. Chem. Journ.*, **2**. 217, 281, 1880 ; M. Guichard, *Bull. Soc. Chim.*, (3), **17**. 902, 1897 ; *Recherches sur les oxydes, les sulfures et les iodures de molybdène*, Paris, 1900 ; *Compt. Rend.*, **125**. 26, 105, 1897 ; **143**. 744, 1906 ; H. E. Quantin, *ib.*, **104**. 223, 1887 ; **106**. 1075, 1888 ; H. Moissan, *ib.*, **125**. 839, 1897 ; C. E. Guignet, *ib.*, **108**. 178, 1889 ; H. Debray, *ib.*, **66**. 732, 1868 ; P. Camboulives, *ib.*, **150**. 175, 1910 ; K. W. G. Kastner, *Kastner's Arch.*, **26**. 465, 1835 ; C. Reichard, *Chem. Ztg.*, **27**. 1, 1903 ; C. F. Rammelsberg, *Pogg. Ann.*, **127**. 281, 1864 ; F. R. M. Hitchcock, *Journ. Amer. Chem. Soc.*, **20**. 232, 1898 ; E. F. Smith, *ib.*, **20**. 289, 1888 ; C. B. Dudley, *ib.*, **15**. 519, 1893 ; O. S. Doolittle and A. Eavenson, *ib.*, **16**. 234, 1894 ; W. A. Noyes and E. D. Frohman, *ib.*, **16**. 553, 1894 ; C. H. Ehrenfeld, *ib.*, **17**. 381, 1895 ; A. A. Blair and J. E. Whitfield, *ib.*, **17**. 747, 1895 ; R. D. Hall, *ib.*, **26**. 1244, 1904 ; E. H. Miller and H. Frank, *ib.*, **25**. 919, 1903 ; H. W. Underwood, *Chem. Met. Engg.*, **29**. 709, 1923 ;

H. N. Warren, *Chem. News*, **60**. 187, 1889; **64**. 75, 1891; **75**. 2, 1897; W. R. E. Hodgkinson and F. K. S. Lowndes, *ib.*, **58**. 309, 1888; E. W. Engle, *Trans. Amer. Electrochem. Soc.*, **51**. 345, 1927; T. S. Patterson and C. Buchanan, *Journ. Chem. Soc.*, 3006, 1928; E. Abel, *Monatsh.*, **28**. 1239, 1907; E. Spitalsky and A. Funck, *Zeit. phys. Chem.*, **126**. 1, 1927; A. Michaelis, *Jena. Zeit.*, **7**. 110, 1871; A. Werncke, *Zeit. anal. Chem.*, **14**. 1, 1875; A. C. Chapman and H. D. Law, *Analyst*, **32**. 250, 1907; D. L. Randall, *Amer. Journ. Science*, (4), **24**. 313, 1907; *Chem. News*, **97**. 113, 1908; E. D. Campbell, *Journ. Anal. Chem.*, **1**. 370, 1887; *Zeit. anal. Chem.*, **28**. 703, 1889; C. Reinhardt, *Chem. Ztg.*, **13**. 323, 1889; W. Scott, *Journ. Ind. Eng. Chem.*, **12**. 575, 1920; P. Sabatier and J. B. Senderens, *Ann. Chim. Phys.*, (7), **7**. 348, 1896; C. Jones, *Trans. Amer. Inst. Min. Eng.*, **90**. 18, 705, 1889; *Chem. News*. **60**. 93, 1889; F. Schrader, *Metalldoppelsalze des Diammoniums und Diamids*, Kiel, 1893; T. Curtius and F. Schrader, *Journ. prakt. Chem.*, (2), **50**. 311, 1893; H. O. Schulze, *ib.*, (2), **21**. 407, 1880; A. Müller, *ib.*, (1), **80**. 119, 1869; A. Geuther, *Liebig's Ann.*, **106**. 239, 1858; H. Schiff, *ib.*, **102**. 116, 1857; G. Rauter, *ib.*, **270**. 236, 1892; E. Darmois, *Bull. Soc. Chim.*, (4), **43**. 1214, 1928; *Trans. Faraday Soc.*, **26**. 384, 1930; W. Muthmann, *Ber.*, **20**. 989, 1887; *Ueber niedere Oxyde des Molybdäns*, München, 1886; *Liebig's Ann.*, **238**. 108, 1887; P. Kulisch, *ib.*, **231**. 327, 1885; *Ueber die Einwirkung des Phosphorwasserstoffs auf Metallsalzlosungen*, Berlin, 1885; J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817; *Pogg. Ann.*, **4**. 153, 1825; **6**. 331, 369, 1826; **7**. 261, 1826; *Ann. Chim. Phys.*, (2), **17**. 5, 1821; C. F. Schönbein, *Ber. Verh. Nat. Ges. Basel*, **8**. 8, 1849; G. E. Uhrlaub, *Pogg. Ann.*, **101**, 605, 1857; *Die Verbindungen einiger Metalle mit Stickstoff*, Göttingen, 20, 1859; H. Rose, *Pogg. Ann.*, **75**. 310, 1847; L. Ott, *Elektrolyse geschmolzener Molybdate und Vanadate*, München, 23, 1911; L. Rolla and G. Piccardi, *Atti Accad. Lincei*, (6), **5**. 546, 1927; A. Michael and A. Murphy, *Amer. Chem. Journ.*, **44**. 365, 1910; A. Chilesotti, *Zeit. Elektrochem.*, **12**. 159, 1906; B. Kalischer, *Zur Kenntnis der Halogenide des höchwertigen Wolframs und Molybdäns*, Berlin, 1902; J. Milbauer, *Zeit. anorg. Chem.*, **42**. 433, 1904; A. Rosenheim and M. Koss, *ib.*, **49**. 148, 1906; R. Abegg and G. Bodländer, *ib.*, **20**. 453, 1899; R. H. Bradbury, *ib.*, **7**. 43, 1894; K. Someya, *ib.*, **138**. 291, 1924; **145**. 168, 1925; **152**. 368, 1926; H. Brintzinger and F. Oschatz, *ib.*, **165**. 221, 1927; C. Killing, *Journ. Gasbelencht.*, **39**. 697, 1897; G. C. Wittstein, *Pharm. Viertelj.*, **9**. 282, 1860; O. F. von der Pfordten, *Liebig's Ann.*, **222**. 137, 1884; M. D. de Plaza, *Anal. Fis. Quim.*, **14**. 542, 1910; L. Fernandes, *Gazz. Chim. Ital.*, **53**. 514, 1923; **55**. 425, 1925; G. A. Barbieri, *Ber.*, **60**. B, 2415, 1927; B. Glassmann, *Ber.*, **38**. 600, 1905; K. Chakravaty and J. C. Ghosh, *Journ. Indian Chem. Soc.*, **4**. 431, 1927; K. Fuwa, *Journ. Japan. Cer. Assoc.*, 129, 1923; L. Kahlenberg and W. J. Trautmann, *Trans. Amer. Electrochem. Soc.*, **39**. 377, 1921; A. Benrath, *Zeit. wiss. Photochem.*, **16**. 253, 1917; E. Berger and L. Delmas, *Bull. Soc. Chim.*, (4), **29**. 68, 1921; G. Bailhache, *Journ. Chem. Soc.*, **82**. ii, 243, 1902; P. Klason, *ib.*, **80**. ii, 162, 1901; F. Göbel, *Bull. Soc. Nat. Moscow*, **9**. 312, 1836; *Journ. prakt. Chem.*, (1), **6**. 386, 1835; J. L. Gay Lussac and L. J. Thénard, *Recherches physicochimiques*, Paris, **1**. 316, 1811; W. H. Rodebush and W. A. Nichols, *Phys. Rev.*, (2), **35**. 649, 1930; E. Wrede, *Zeit. Physik*, **41**. 569, 1927; C. Boulanger, *Compt. Rend.*, **191**. 56, 1930; R. Wasmuth, *Zeit. angew. Chem.*, **43**. 98, 125, 1930; D. Balareff and N. Lukowa, *Koll. Zeit.*, **52**. 222, 1930; S. Ghosh and A. K. Bhattacharya, *Journ. Indian Chem. Soc.*, **7**. 717, 1930; W. Jakob and W. Koslowsky, *Rocz. Chem.*, **9**. 667, 1929; D. D. Peirce and L. F. Yntema, *Journ. Phys. Chem.*, **34**. 1822, 1930; R. Hac and V. Netuka, *Coll. Czechoslow. Chem. Comm.*, **1**. 521, 1929; G. Cannerei, *Gazz. Chim. Ital.*, **60**. 113, 1930; O. Ruff and H. Krug, *Zeit. anorg. Chem.*, **190**. 270, 1930; J. A. Hedvall and N. von Zweigbergh, *Zeit. anorg. Chem.*, **108**. 119, 1919.

[6] T. Graham, *Journ. Chem. Soc.*, **17**. 318, 1864; *Phil. Mag.*, (4), **28**. 314, 1864; *Proc. Roy. Soc.*, **13**. 335, 1864; *Compt. Rend.*, **59**. 174, 1864; A. Sabanéeff, *Journ. Russ. Phys. Chem. Soc.*, **21**. 515, 1891; **22**. 102, 1891; S. J. Diatschkovsky and A. V. Dumansky, *ib.*, **58**. 630, 1926; A. V. Dumansky, A. P. Buntin, S. J. Diatschkovsky and A. G. Knicja, *ib.*, **58**. 326, 1926; *Koll. Zeit.*, **38**. 208, 1926; G. Bruni and N. Pappada, *Atti Accad. Lincei*, (5), **9**. i. 354, 1900; *Gazz. Chim. Ital.*, **31**. i, 244, 1901; A. Rosenheim and I. Davidsohn, *Zeit. anorg. Chem.*, **37**. 314, 1903; A. Rosenheim and A. Bertheim, *ib.*, **34**. 427, 1903; A. Rosenheim, *ib.*, **50**. 320, 1906; L. Wöhler, *Zeit. Elektrochem.*, **16**. 639, 1910; L. Wöhler and W. Engels, *Koll. Beihefte*, **1**. 454, 1910; R. Wintgen, *ib.*, **7**. 251, 1915; F. Ullik, *Sitzber. Akad. Wien*, **55**, 767, 1867; *Liebig's Ann.*, **144**. 204, 320, 1867; G. Wegelin, *Koll. Zeit.*, **14**. 65, 1914; W. Reinders, *ib.*, **13**. 235, 1913; A. Lottermoser, *Ueber anorganische Colloide*, Stuttgart, 11, 1901; C. E. Linebarger, *Amer. Journ. Science*, (3), **43**. 222, 1892; H. Picton and S. E. Linder, *Journ. Chem. Soc.*, **61**. 155, 1892; D. N. Chakravarti and N. R. Dhar, *Koll. Zeit.*, **42**. 124, 1927; L. S. Bhatia, S. Ghosh and N. R. Dhar, *Zeit. anorg. Chem.*, **184**. 135, 1929; S. Ghosh and N. R. Dhar, *ib.*, **190**. 421, 1930; E. F. Krause and A. V. Novoseloff, *Journ. Russ. Phys. Chem. Soc.*, **62**. 287, 1930; W. V. Bhagwat and N. R. Dhar, *Journ. Indian Chem. Soc.*, **6**. 781, 807, 1929; W. von Behren and J. Traube, *Zeit. phys. Chem.*, **146**. 1, 1930.

[7] C. Hatchett, *Phil. Trans.*, **95**. 323, 1795; J. H. Graham, *Journ. Franklin Inst.*, **163**. 69, 1907; *Chem. News*, **96**. 262, 1907; T. Graham, *Compt. Rend.*, **59**. 174, 1864; *Proc. Roy. Soc.*, **13**. 335, 1864; *Journ. Chem. Soc.*, **17**. 318, 1864; Phil. Mag., (4), **28**. 314, 1864; C. F. Bucholz, *Scherer's Journ.*, **9**. 485, 1802; *Gehlen's Journ.*, **4**. 598, 1805; *Phil. Mag.*, **16**. 193, 1803; H. Debray, *Compt. Rend.*, **45**. 1020, 1857; J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817; *Pogg. Ann.*, **4**. 153, 1825; **6**. 331, 369, 1826; **7**. 261, 1826; *Ann. Chim. Phys.*, (2), **17**. 5, 1821; F. Ullik, *Sitzber. Akad. Wien*, **55**. 767, 1867; *Liebig's Ann.*, **144**. 204, 320, 1867; H. C. Burger, *Zeit. anorg. Chem.*, **121**. 240, 1922; L. S. Bhatia, S. Ghosh and N. R. Dhar, *ib.*, **184**. 135, 1929;

A. Rosenheim and I. Davidsohn, *ib.*, **37**. 314, 1903 ; A. Rosenheim and A. Bertheim, *ib.*, **34**. 427, 1903 ; A. Rosenheim, *ib.*, **36**. 752, 1903 ; **50**. 320, 1906 ; G. F. Hüttig and B. Kurre, *ib.*, **126**. 167, 1923 ; G. F. Hütting, *Zeit. angew. Chem.*, **35**. 391, 1922 ; L. C. A. Vivier, *Compt. Rend.*, **106**. 601, 1888 ; F. Parmentier, *ib.*, **95**. 839, 1882 ; L. Forsén, *ib.*, **172**. 215, 327, 681, 1921 ; A. A. Blair and J. E. Whitfield, *Journ. Amer. Chem. Soc.*, **17**. 747, 1895 ; A. de Schulten, *Bull. Soc. Min.*, **26**. 6, 1903 ; M. Jungek, *Zeit. anal. Chem.*, **15**. 290, 1876 ; S. Kern, *Chem. News*, **37**. 98, 1878 ; J. Terwelp, *Beiträge zur Elektrochemie der Molybdate*, Berlin, 21, 1903 ; M. Briand, *Ueber Molybdate, Sulfomolybdate und Phosphormolybdate des Lithiums*, Bern, 31, 1905 ; F. Ephraim and M. Brand, *Zeit. anorg. Chem.*, **64**. 258, 1909 ; E. Müller, *ib.*, **33**. 182, 1927 ; A. Mazzucchelli and G. Zangrilli, *Gazz. Chim. Ital.*, **40**. ii, 49, 1910 ; A. Mazzucchelli and M. Borghi, *ib.*, **40**. ii, 254, 1910 ; *Atti Accad. Lincei*, (5), **19**. ii, 439, 1910 ; F. Mylius, *Ber.*, **36**. 638, 1903 ; H. H. Willard and F. Fenwick, *Journ. Amer. Chem. Soc.*, **45**. 928, 1923 ; O. Tomicek, *Rec. Trav. Chim. Pays-Bas*, **43**. 788, 1914 ; K. von der Heide, *Ueber Verbindungen niederen Molybdänoxyde und -sulfide mit Ammoniak und Cyankalium*, München, 1897 ; E. Darmois and A. Honnelaitre, *Compt. Rend.*, **178**. 2183, 1924 ; E. Rimbach and P. Ley, *Zeit. phys. Chem.*, **100**. 393, 1922 ; A. Honnelaitre, *Ann. Chim. Phys.*, (10), **3**. 5, 1925 ; A. Travers and L. Malaprade, *Compt. Rend.*, **183**. 292, 533, 1926 ; *Bull. Soc. Chim.*, (4), **39**. 1408, 1926 ; R. F. Weinland and F. Geisser, *Zeit. anorg. Chem.*, **108**. 231, 1919 ; R. F. Weinland and K. Zimmermann, *ib.*, **108**. 248, 1919 ; R. F. Wienland, A. Babel, K. Cross and H. Mai, *ib.*, **150**. 177, 1926 ; R. F. Wienland and P. Muthmann, *Arch. Pharm.*, **262**. 329, 1924 ; S. I. Diatschkovsky and A. V. Dumansky, *Journ. Russ. Phys. Chem. Soc.*, **58**. 630, 1926 ; R. Hac and V. Netuka, *Coll. Czech. Chem. Comm.*, **1**. 521, 1929 ; E. F. Krauze and A. V. Novoseloff, *Journ. Russ. Phys. Chem. Soc.*, **62**. 287, 1930 ; G. Jander, K. F. Jahr, and W. Heukeshoven, *Zeit. anorg. Chem.*, **194**. 383, 1930 ; G. Jander and W. Heukeshoven, *ib.*, **187**. 60, 1930.

§ 11. The Monomolybdates—Normal Molybdates

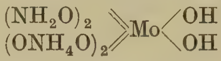
The action of liquid ammonia on molybdenum trioxide furnishes amides and imidies as indicated **8**. 49, 21. Normal **ammonium molybdate,** $(NH_4)_2MoO_4$, crystallizes from conc. soln. of molybdenum trioxide in warm, conc., aq. ammonia during cooling, or on the addition of alcohol. The salt was obtained in this way by L. F. Svanberg and H. Struve,[1] J. C. G. de Marignac, F. A. Flückiger, and A. Rosenheim. A. Werncke obtained it from the mother-liquor in the preparation of ammonium phosphomolybdate ; and A. S. Garnak described a method of preparing the salt from ferromolybdenum. Analyses in accord with the formula were made by L. F. Svanberg and H. Struve, F. A. Flückiger, A. Werncke, and G. Wempe. L. F. Svanberg and H. Struve described the crystals as four-sided prisms. J. C. G. de Marignac found that the monoclinic prisms have the axial ratios $a : b : c = 1{\cdot}9542 : 1 : 1{\cdot}2066$, and $\beta = 117° \ 45'$. Observations were also made by W. Keferstein ; and G. N. Wyrouboff said that the crystals are isomorphous with those of ammonium chromate, and J. W. Retgers, with those of ammonium selenate and chromate. J. W. Retgers added that ammonium chromate, selenate, and molybdate are isodimorphous with potassium sulphate. H. Schröder gave 2·270 for the sp. gr. According to J. C. G. de Marignac, the crystals effloresce rapidly in air owing to the loss of ammonia ; F. A. Flückiger said that if the crystals are freed from the mother-liquor they are stable in air. L. F. Svanberg and H. Struve found that the crystals are unstable in contact with water and rapidly form an acid salt. T. L. Phipson found that the aq. soln. is decomposed in sunlight and R. E. Liesegang observed that in light, the salt is decomposed with the separation of a blue oxide. The change can be followed titrimetrically so that the soln. can be used as a kind of actinometer. The presence of organic substances, like lactic acid, makes the liquid more sensitive to light ; some salts favour and others retard the action. In darkness the original colour is restored by the oxidizing action of the air—*vide supra*, molybdic acid and alcohol. P. Krishnamurti studied the Raman effect. W. V. Bhagwat and N. R. Dhar found the eq. electrical conductivity of ammonium molybdate to be for an eq. of the salt in v litres, at 21°,

v . .	16	32	64	128	256	512	1024
λ . .	84·5	96·45	108·8	120·3	128·6	136·9	143·5

so that $\mu_{1024} - \mu_{32} = 47{\cdot}05$.

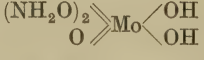
F. Krauss and E. Bruchhaus found that ammonium molybdate in aq. soln., and exposed to rays of short wave-length, is reduced by hydrogen. For the hydrolysis of aq. soln., *vide infra*, ammonium paramolybdate. J. W. Thomas found that the salt is decomposed by hydrochloric acid; H. P. Cady and R. Taft, that ammonium molybdate is insoluble in liquid sulphur dioxide; H. Stamm measured its solubility in aq. ammonia and found that soln. with 0·170, 1·192, 1·750, and 3·382 mols of NH_3 per 100 grms. of water dissolved respectively 0·333, 0·268, 0·231, and 0·187 mol of $(NH_4)_2MoO_4$. O. Brunck observed that sodium hyposulphite precipitates molybdenum sulphide from acid soln; and F. J. Faktor, that sodium thiosulphate reduces a soln. of the molybdate to hydrated dioxide, and trioxide; and I. F. J. Kupfferschläger, that an excess of nitric acid gives a precipitate with a conc. aq. soln. A soln. of ammonium molybdate with an excess of nitric acid is used as a reagent for the detection of phosphoric acid. P. Kulisch disagreed with A. Winkler's statement that phosphine does not reduce soln. of ammonium molybdate—only in the absence of free acid is a soln. of the molybdate little affected by phosphine. O. F. von der Pfordten obtained a dark brown precipitate on adding a soln. of titanium dichloride to a soln. of the molybdate; and this is oxidized to a white mass in air. C. E. Guignet observed that the soln. of the molybdate dissolves prussian blue; and S. M. Jörgensen that it gives a precipitate with chromic chloropentamminochloride.

No normal **hydroxylamine molybdate** has yet been prepared. G. Canneri[2] observed that hydroxylamine added to a soln. of a paramolybdate forms a red soln. which deposits yellow molybdic molybdates. If hydroxylamine chloride be added to a hot, aq. soln. of alkali molybdate, and the precipitate be washed successively with water, alcohol, and ether, the following salts are formed: yellow **ammonium hydroxylamine paramolybdate,** $(NH_4)_2O.4NH_2OH.4MoO_3$; yellow **potassium hydroxylamine paramolybdate,** $K_2O.4NH_2OH.4MoO_3$; yellow **sodium hydroxylamine paramolybdate,** $Na_2O.4NH_2OH.4MoO_3$; and similarly with the guanidine salt. V. Kohlschütter and K. A. Hofmann found that **potassium hydroxylaminopentahydromolybdate,** $MoO_4H_2(NH_2OH)_3(NH_2OK)$—*vide infra*—is obtained as a salt of what they supposed to be the acid



$$\begin{matrix}(NH_2O)_2\\(ONH_4O)_2\end{matrix}\!\!>\!Mo\!<\!\begin{matrix}OH\\OH\end{matrix}$$

by mixing aq. soln. of ammonium molybdate (5 grms.), hydroxylamine hydrochloride (10 grms.), and potassium carbonate, and adding alcohol to the yellow soln. The salt reduces Fehling's soln., or ammoniacal silver nitrate; it decomposes when heated forming a black powder with the liberation of ammonia. The salt dissolves in water, and when the pale yellow, neutral, aq. soln. is treated with carbon dioxide, hydroxylaminomolybdic acid separates as a yellowish-white, flocculent precipitate. If ammonium molybdate (10 grms.) and hydroxylamine hydrochloride (7 grms.) be mixed with 50 c.c. of 7 per cent. aq. ammonia at 8°, a compound is formed which dissolves with difficulty in water; and develops a bluish-green coloration when heated with dil. sulphuric acid. The composition of the product is $MoO_5N_3H_9$, and it is regarded as **dihydroxylamine amminomolybdate,** $MoO_5N_3H_9$, or $MoO_3(NH_2OH)_2NH_3$, a salt of what they suppose to be the acid:



$$\begin{matrix}(NH_2O)_2\\O\end{matrix}\!\!>\!Mo\!<\!\begin{matrix}OH\\OH\end{matrix}$$

C. F. Rammelsberg[3] obtained **lithium molybdate,** $Li_2MoO_4.\frac{2}{5}H_2O$ (A. Rosenheim and W. Reglin find $Li_2MoO_4.\frac{3}{4}H_2O$), by boiling a mol each of lithium carbonate and molybdenum trioxide, and allowing the filtrate to crystallize. G. Wempe obtained the salt in a similar way; and M. Delafontaine, by fusing equimolar proportions of lithium carbonate and molybdenum trioxide, and allowing the syrupy aq. soln. to stand some days. F. Hoermann measured the f.p. curves of

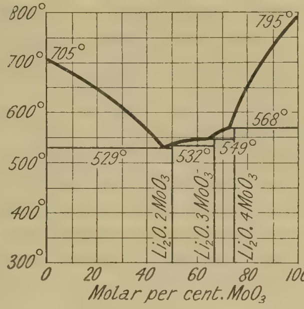


FIG. 13.—Equilibrium Curves of the System : Li_2MoO_4–MoO_3.

the system : Li_2MoO_4–MoO_3, and the results are summarized in Fig. 13. The existence of three unstable acid salts is indicated, namely, lithium di-, tri-, and tetramolybdate. W. Zachariassen found that the X-radiogram of Li_2MoO_4 agrees with a unit cell having 6 mols. and with the dimensions a=8·20 A., c=9·45 A., and $a : c$=1 : 1·153 ; and that the salt is isomorphous with phenacite, willemite, lithium tungstate, and lithium fluoberyllate. F. Ephraim and M. Brand suggest that the water in the *pentitadihydrate* prepared by both processes is merely hygroscopic moisture. M. Delafontaine also obtained the *tritoctohydrate*, $Li_2MoO_4.2\frac{2}{3}H_2O$, in monoclinic or triclinic crystals, from a soln. of an acid molybdate sat. with lithium carbonate. The prismatic crystals of the pentitadihydrate are fairly stable in air but they are hygroscopic. G. Wempe said that 100 c.c. of the aq. soln. sat. at 20° contains 46·13 grms. of the hydrated salt and has a sp. gr. of 1·44. F. Ephraim and M. Brand found that the salt is only a little more soluble in hot than in cold water. F. Hoermann gave 705° for the m.p. of the salt. A. Rosenheim and W. Reglin found the solubility of $Li_2MoO_4.\frac{3}{4}H_2O$, S grms. Li_2MoO_3 per 100 grms. of soln., to be :

	0°	25°	30°	40°	98°
S . .	45·24	44·81	44·26	43·84	42·50

so that the temp. coeff. is negative. A. Rosenheim and W. Reglin also found that the salt dissolves readily in a soln. of lithium hydroxide, and on evaporating the liquid, non-crystallizable syrups are formed. Solubility is less as the temp. rises. The aq. soln. has an alkaline reaction. The aq. soln. of a mol of the salt and 5 mols of ammonium chloride yields crystals of ammonium paramolybdate free from lithium. The eq. conductivity, λ mhos, of a mol of the normal salt in v litres of water, at 20°, was found by G. Wempe to be :

v . .	10	20	40	80	160	320
λ . .	422	524	604	664	736	800

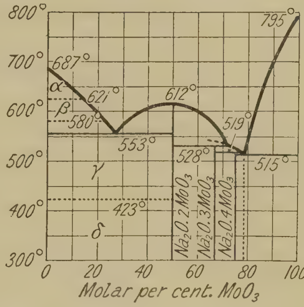


FIG. 14.—Equilibrium Curves of the System : Na_2MoO_4–MoO_3.

L. F. Svanberg and H. Struve obtained anhydrous **sodium molybdate**, Na_2MoO_4, by melting together equimolar parts of molybdenum trioxide and sodium carbonate, and cooling the mass. The salt obtained by heating the hydrate to 100° was found by J. G. Gentele, and F. E. Zenker to furnish a molten mass which cools to an opaque, white enamel of the anhydrous salt. F. Hoermann measured the f.p. curves of the system : Na_2MoO_4–MoO_3, and the results are summarized in Fig. 14. The existence of three acid salts is indicated, namely, sodium di-, tri-, and tetra-molybdate. E. Groschuff obtained a similar curve. The monomolybdate exists in four modifications. The α-form is stable above about 620° ; the β-form is stable between 620° and 580° ; the γ-form between 580° and 410° ; and the δ-form below 410°. For the $\alpha \rightleftharpoons \beta$, $\beta \rightleftharpoons \gamma$, and $\gamma \rightleftharpoons \delta$ transition temp. K. Hüttner and G. Tammann observed transformations respectively between 620° and 605°, and 410° and 380° ; H. E. Boeke gave for the three transformation temp. respectively 619°, 587°, and 431° ; E. Groschuff, 609°, 575°, and 408°—Fig. 14 ; H. S. van Klooster, 626°, 580°, and 397° ; F. Hoermann, 621°, 580°, and 423° ; and M. Amadori, 616°, 580°, and 410° when all are taken on a cooling curve. H. S. van Klooster found on a heating curve the respective values 640°, 592°, and 445°, showing that the transition temp. are overstepped. A. Hare gave 440° for the last transformation temp. The subject is still further discussed in connection with sodium tungstate. With 10 per cent. of molybdenum trioxide associated with the sodium molybdate, E. Groschuff found the transition temp. are changed respectively to 614°, 567°, and 412°. H. E. Boeke found that with 0·055, 0·40, and 3·00 molar per cent. of Na_2SO_4, the $\gamma \rightleftharpoons \delta$ transition temp. is lowered from 431° respectively to 396°, 297°, and about 180°. This depression is much greater than that calculated from the heat of the transformation, 3·33 Cals., and the anomaly is explained by H. S. van Klooster by assuming that the presence of sodium sulphate considerably augments the speed of the transformation. H. E. Boeke found that the binary system Na_2SO_4–Na_2MoO_4 forms a continuous series of solid soln. on solidification. There is a minimum in the f.p. curve, Fig. 15. For the binary system: Na_2WO_4–Na_2MoO_4, and the ternary system: Na_2SO_4–Na_2WO_4–Na_2MoO_4, *vide* sodium tungstate.

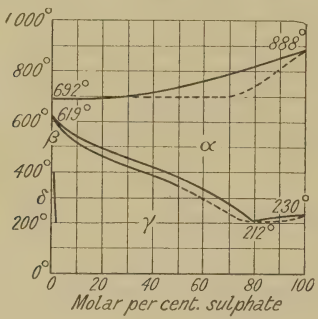


Fig. 15.—Binary System: Na_2MoO_4–Na_2SO_4.

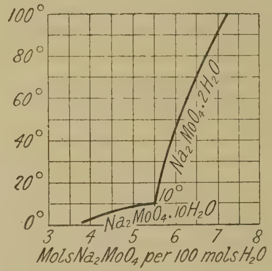


Fig. 16.—Solubility Curve of Sodium Molybdate.

The equilibrium conditions in the ternary system: Na_2O–MoO_3–H_2O have not been worked out. R. Funk's solubility curve, Fig. 16, shows that within the range of temp. 0° to 100°, there are two hydrates: $Na_2MoO_4.10H_2O \rightleftharpoons Na_2MoO_4.2H_2O + 8H_2O$ with a transition at about 10°. L. F. Svanberg and H. Struve obtained the *dihydrate* by crystallizing an aq. soln. of the anhydrous salt, and drying the crystals for 24 hrs. over lime and sulphuric acid. F. E. Zenker evaporated an aq. soln. of the paramolybdate mixed with an excess of sodium hydroxide; F. Ullik, an aq. soln. of the acid or an acid salt sat. with sodium carbonate; M. Delafontaine used a similar process; and J. G. Gentele allowed the decahydrate to effloresce in the cold. According to M. Delafontaine, the rectangular or rhombic plates or scales are probably isomorphous with the crystals of normal tungstate. They lose all their water at 100°. The molten mass does not expel carbon dioxide from sodium carbonate. R. Funk found the solubility, *S* grms. of Na_2MoO_4 per 100 grms. of solution, to be:

	0°	4°	6°	9°	10°	32°	51·5°	100°
S .	30·63	33·83	35·58	38·16	39·28	39·82	41·27	45·57
	$Na_2MoO_4.10H_2O$.					$Na_2MoO_4.2H_2O$.		

The results are plotted in Fig. 16. The transition temp. is near 10°. J. G. Gentele obtained the *decahydrate* by evaporating the aq. soln. between 0° and 6°. The columnar crystals have the appearance of Glauber's salt. The crystals effloresce at about 6°, and are stable below that temp. In a closed vessel, at room temp., the crystals become opaque and gradually form the scaly crystals of the dihydrate. M. Delafontaine could not prepare the decahydrate.

G. Beck gave 3·28 for the sp. gr. of the salt, and 62·0 for the mol. vol. F. M. Jäger measured the sp. gr. of the molten salt—D referred to water at 4°—and found:

	698·5°	751°	818·8°	903·8°	989·5°	1078·5°	1171·5°
D .	2·796	2·763	2·720	2·667	2·613	2·557	2·499
σ .	214·0	208·1	202·4	195·4	187·7	181·2	176·1
χ .	376·1	3686	3623	3544	3451	3380	3335

The results for the sp. gr. between 700° and 1171° can be represented by $D=2·795-0·000629(\theta-700)$—*vide infra*, electrical resistance. W. Herz made some observations on this subject. I. Traube found the sp. gr., D, and mol. soln. vol., v, of aq. soln. of the salt, at 15°, to be:

Na_2MoO_4	6·31	11·84	19·91	22·18 per cent.
D . .	1·0555	1·1085	1·1928	1·2194
v . .	32·9	34·4	38·1	38·3

R. Lorenz and W. Herz studied the relation between the critical densities of related salts, and they also found that the surface tension at the m.p. and b.p. are respectively 215·5 and 177·9; G. Jander and co-workers studied the diffusion; and I. Traube found 232 for the drop-weight of molten sodium molybdate when the value for water at 0° is 100. F. M. Jäger's values for the surface tension, σ dynes per cm., and the surface energy, χ ergs per sq. cm., of the molten salt, are indicated above. J. J. Coleman found that 28, 25, and 17 per cent. of normal soln. of sodium molybdate, chromate, and tungstate, respectively, diffused in water 75 mm. in 30 days at 12·5°. W. Herz gave 0·0002752 for the coeff. of thermal expansion. G. Tammann found the lowering of the vap. press. per 100 grms. of water to be 24·4, 73·2, and 166·9 mm., respectively. The m.p. of the anhydrous salt was found to be 692° by K. Küttner and G. Tammann, and H. E. Boeke; 687°, by L. I. Dana and P. D. Foote; 688°, by M. Amadori; 685°–687°, by H. S. van Klooster; and 686°, by E. Groschuff. The fusion curve with sodium sulphate mixtures is shown in Fig. 15. E. Darmois and J. Périn found that the mol. wt. is normal when calculated from its effect on the f.p. of decahydrated sodium sulphate. R. Lorenz and W. Herz studied the relation between the b.p. and the critical temp. W. G. Mixter gave for the heat of formation $(Na_2O,Mo,3O)=263·4$ Cals.; $(Na_2O,MoO_2,O)=120·6$ Cals.; and $(Na_2O,MoO_3)=81·936$ Cals. A. Hare gave 14·6 Cals. per mol for the heat of transformation at about 440°. L. Pissarjewsky found for the thermal value of the reaction: $H_2MoO_{4\text{soln.}}+2NaOH=Na_2MoO_{4\text{soln.}}+2H_2O+21·728$ Cals. A. Hare gave 14·60 Cals. per mol for the heat of the transformation at 440°.

F. M. Jäger and B. Kapma found the resistance, R ohms, of fused sodium molybdate to be:

	843°	924·5°	1026°	1122·5°	1217°	1306°	1408°
R . .	0·1256	1·1105	0·0948	0·0842	0·0752	0·0690	0·0620
Sp. gr. .	2·705	2·654	2·590	2·529	2·470	2·414	2·350

and they represented the mol. conductivity, μ, at θ° between 543° and 1408°, by $\mu=107·50+0·183(\theta-850)$. P. Walden found the eq. conductivity, λ mhos, of soln. of an eq. of sodium molybdate in v litres of water at 25°, to be:

v . . .	32	64	128	256	512	1204
λ . . .	100·5	106·1	111·0	114·6	117·8	120·8

H. Crossmann gave $\mu_{1024}-\mu_{32}=22·4$ at 25°. J. Terwelp obtained similar results, and he found the transport number of the MoO_4''-ion in $0·1N$-Na_2MoO_4 to be 0·58 at 18°. G. Jander and co-workers studied the electrometric titration of the salt. L. Ott found the decomposition voltage of the fused salt to be 1·15 volt; and the cathode deposit is MoO_2 as well as some metal. J. Terwelp, and A. Junius found that the electrolysis of neutral aq. soln. of sodium molybdate without diaphragms, does not produce very marked change since the diffusion of the anodic and cathodic products restores the original state of things. A cathodic reduction occurs only in acidic soln. In a diaphragmed cell, paramolybdate and trimolybdate appear to be formed in the anode compartment—*vide supra*, molybdenum trioxide. The aq. soln. was found by F. E. Zenker, and A. Junius to react acid; but the hydrolysis cannot be very marked because K. Seubert and W. Pollard found that a soln. of molybdic acid can be sharply titrated with a soln. of sodium hydroxide using litmus or phenolphthalein as indicator—*vide infra*, ammonium paramolybdate. F. Ullik found that the soln. of sodium molybdate is not reduced by tin.

F. Hoermann found that the f.p. curve of mixtures of lithium and sodium molybdates, Fig. 17, showed the existence of an unstable **lithium sodium molybdate,** $Li_2MoO_4.3Na_2MoO_4$.

L. F. Svanberg and H. Struve prepared **potassium molybdate,** K_2MoO_4, by evaporating for crystallization a soln. of molybdic acid or an acid molybdate in an excess of potassium hydroxide or carbonate. J. Ohly said that the product is then liable to be contaminated with potassium carbonate. The formation of the acid molybdate can be avoided only by using an excess of alkali. L. F. Svanberg and H. Struve treated an acid molybdate with soln. of potassium hydroxide in 95 per cent. alcohol. The oil which separates was washed with alcohol and allowed to crystallize first over lime and then sulphuric acid. F. Ullik fused equimolar parts of molybdenum trioxide and potassium carbonate, dissolved the product in hot water, and allowed the filtered soln. to cool. L. F. Svanberg and H. Struve supposed the crystals to be hemihydrated; and F. Ullik thought they are anhydrous. M. Delafontaine could not prepare this salt. M. Amadori found that anhydrous potassium molybdate separates from its aq. soln. at 25°; and the salt remains anhydrous in contact with water at this temp. G. Wempe reported a *tetritatrihydrate*, $K_2MoO_4.\frac{3}{4}H_2O$, to be formed by filtering a boiling soln. of molybdic acid in a conc. soln. of potassium carbonate, allowing the filtered liquid to cool on a glass plate, and separating mechanically the crystals from the amorphous, gum-like mass. The salt loses its water at 120°. F. Hoermann studied the f.p. curve of the system: K_2MoO_4–MoO_3, and the results, summarized in Fig. 18, show the existence of a dimolybdate only.

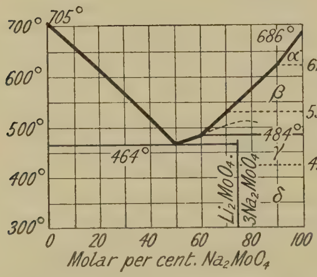


Fig. 17.—The Equilibrium Curves of the System: Li_2MoO_4–Na_2MoO_4.

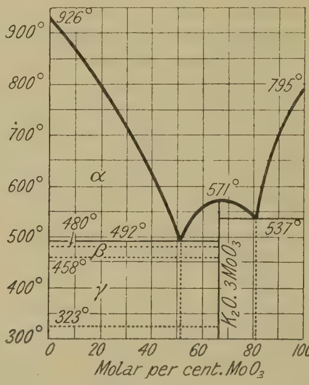
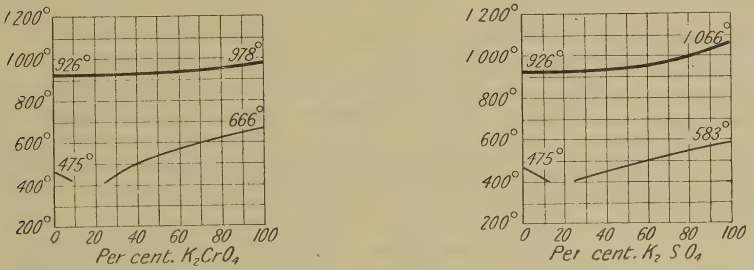


Fig. 18.—Equilibrium Curves of the System: K_2MoO_4–MoO_3.

L. F. Svanberg and H. Struve said that the crystals of potassium molybdate, K_2MoO_4, are four-sided prisms. H. S. van Klooster observed that the cooling salt undergoes three transformations: there is the $\alpha \rightleftharpoons \beta$ change at 479°; the $\beta \rightleftharpoons \gamma$ change at 454°; and the $\gamma \rightleftharpoons \delta$ change at 327°; M. Amadori gave 475° for the $\alpha \rightleftharpoons \beta$ change; and K. Hüttner and G. Tammann, 200° for the $\gamma \rightleftharpoons \delta$ change. F. Hoermann gave respectively 480°, 458°, and 323°. J. W. Regters observed that during the crystallization of potassium molybdate there are formed acicular crystals supposed to be rhombic or pseudohexagonal and isomorphous with potassium permanganate; and prismatic crystals not isomorphous with the salt, and supposed to be monoclinic. M. Amadori found that mixtures of potassium sulphate and molybdate, and of potassium chromate and molybdate have the following f.p. and $\beta \rightleftharpoons \alpha$ transition points:

K_2MoO_4		100	80	70	40	20	0 per cent.
K_2SO_4	F.p.	920°	920°	934°	980°	1018°	1066°
	Tr.p.	475°	—	484°	525°	558°	583°
K_2CrO_4	F.p.	926°	926°	934°	942°	960°	976°
	Tr.p.	475°	—	502°	575°	620°	666°

The curve, Fig. 19, for the K_2MoO_4–K_2SO_4 is continuous, and it has a very flat minimum 6° below the m.p. of the molybdate, and the m.p. of the mixture with 45 per cent. of sulphate is equal to that of the molybdate alone. The curve, Fig. 20, for the K_2MoO_4–K_2CrO_4 system is continuous, and with mixtures up to 30 molar per cent. of chromate the f.p. is at the f.p. of the molybdate. M. Amadori also found the solubility isotherm of potassium sulphate and molybdate is similar to that with potassium sulphate and chromate. There is a continuous series of solid soln. in which the more soluble salt is in greater proportion in the soln. than in the crystals; similarly also with the solubility isotherm of mixtures of potassium chromate and molybdate. G. Beck gave 2·91 for the sp. gr. of the salt, and 81·8 for the mol. vol. F. M. Jäger gave the following values for the sp. gr., D, of fused potassium molybdate referred to water at 4°:



FIGS. 19 and 20.—Freezing-point Curves of the Binary System: K_2MoO_4–K_2SO_4 and K_2MoO_4–K_2CrO_4.

	930·6°	1021°	1143°	1273°	1356°	1452°·8
D	2·362	2·307	2·230	2·144	2·087	2·018
σ	150·5	145·2	138·6	130·0	123·6	116·9
χ	3261	3196	3120	3004	2908	2813

and he represented the sp. gr. at $\theta°$ between 694° and 1452° by $D=2{\cdot}342-0{\cdot}0006(\theta-964)-0{\cdot}000000128(\theta-964)^2$. W. Herz made some observations on this subject. I. Traube gave for the sp. gr., D, and mol. soln. vol., v, of aq. soln. of potassium molybdate at 15°:

K_2MoO_4	2·02	6·76	7·37	15·94 per cent.
D	1·0154	1·0548	1·0602	1·1381
v	49·7	52·4	52·2	56·4

I. Traube gave 198 for the drop-weight of the molten salt when that of water at 0° is 100. F. M. Jäger found the results indicated above for the surface tension, σ dynes per cm., and the surface energy, χ ergs per sq. cm. R. Lorenz and W. Herz gave for the surface tensions at the m.p. and b.p. respectively 161·5 and 108·3. G. Jander and A. Winkel gave for the diffusion coeff. of the anion 0·58; and they found the range of stability for $[H^{\cdot}]$ to be 10^{-14} to $10^{-6\cdot2}$. K. Hüttner and G. Tammann, and M. Amadori gave 926° for the m.p. of the salt, and H. S. van Klooster, 919°. The lowering of the vap. press. when 19·62, 56·06, and 111·13 grms. of potassium molybdate are dissolved in 100 grms. of water was found by G. Tammann to be respectively 24·6, 85·3, and 197·1 mm. R. Lorenz and W. Herz studied the relation between the b.p. and the critical temp. P. Blackman found the conductivity of soln. of an eq. of the salt in v litres at 25° to be :

v . .	32	64	128	256	512	1024
λ . .	123	129	133	138	140	144

Measurements by W. V. Bhagwat and N. R. Dhar corresponded with $\mu_{1024}-\mu_{32}=24$. E. Blanc found that there is a 0·359 per cent. hydrolysis with a 0·00975N-soln. of potassium molybdate. L. F. Svanberg and H. Struve, and F. Ullik found that the salt effloresces in moist air, and, attracting carbon dioxide from the atmosphere, forms other salts. M. Amadori observed that a sat. aq. soln. at 25° contains 64·86 per cent. K_2MoO_4. Expressing solubilities in millimols per litre, the solubility, S, of potassium sulphate in the presence of potassium molybdate is :

K_2MoO_4 .	69·88	49·04	22·65	12·21	8·60	4·13	0·00
K_2SO_4 .	0·00	19·85	73·35	192·6	417·5	742·8	774·7

and of potassium chromate in the presence of potassium molybdate :

K_2MoO_4 .	332·3	204·7	72·68	36·66	25·31	8·74	0·00
K_2CrO_4 .	0·00	162·0	414·3	578·1	694·1	767·9	774·7

L. F. Svanberg and H. Struve found potassium molybdate to be insoluble in alcohol ; and to be precipitated by alcohol from the aq. soln. as an oily liquid.

F. Hoermann studied the f.p. curve of mixtures of lithium and potassium molybdates, and found the existence of **lithium potassium molybdate,** $Li_2MoO_4.K_2MoO_4$, with a m.p. at 571°. F. Ullik prepared **potassium sodium molybdate,** $K_2O.2Na_2O_3.MoO_3.14H_2O$, or $K_{\frac{2}{3}}Na_{\frac{4}{3}}MoO_3.4\frac{2}{3}H_2O$, by treating a potassium trimolybdate with water and sodium carbonate. F. Ullik fused molybdenum trioxide with sodium and potassium carbonates, and allowed an aq. soln. of the cold mass to crystallize. J. C. G. de Marignac described the crystals as dihexagonal bipyramidal with the axial ratios $a:c=1:1·2839$. M. Delafontaine stated that all the water is expelled at 100° ; and the salt fuses at a red-heat ; fused sodium carbonate does not lose carbon dioxide when treated with the salt. F. Ullik found that the salt is soluble in cold water, but more easily soluble in hot water ; the soln. has an alkaline reaction.

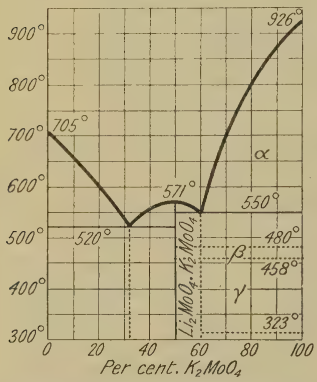


FIG. 21.—Equilibrium Curve of the System : K_2MoO_4–Li_2MoO_4.

A. Piccini [4] prepared normal **rubidium molybdate,** Rb_2MoO_4, by calcining rubidium molybdenum trioxytetrafluoride, $2RbF.MoO_3F_2.H_2O$; and F. Ephraim and H. Herschfinkel obtained the salt by evaporating a soln. of molybdenum trioxide in rubidium hydroxide, and washing the deliquescent mass with alcohol. J. W. Retgers made a few observations on the crystals of **cæsium molybdate,** Cs_2MoO_4.

No **cuprous molybdates** have yet been prepared ; and normal **copper molybdate,** $CuMoO_4$, is not known. H. Debray [5] obtained, possibly, the normal molybdate by roasting cupric sulphomolybdate at a low temp. G. Tammann noted that the reaction between cupric oxide and molybdenum trioxide begins about 615°, and the heat of formation of $CuMoO_4$ is 9·2 Cals. per mol ; J. J. Berzelius observed that a yellowish-green precipitate is produced by potassium molybdate in soln. of copper salts. The precipitate is sparingly soluble in water, and is decomposed by acids and alkali-lye. H. Struve prepared **copper oxymolybdate,** $CuO.3CuMoO_4.5H_2O$, by precipitation from a boiling soln. of copper sulphate by a conc. soln. of ammonium 2 : 5 : 3-molybdate. The green, amorphous powder loses 3 mols. of water at 100°, and the remainder at a higher temp. The dehydrated salt gradually recovers its combined water when in contact with water. According to G. Jörgensen, if sodium molybdate be treated with an excess of a soln. of copper sulphate, and the light green precipitate be dissolved in aq. ammonia, and the soln. treated with alcohol, dark blue needles of **copper tetramminomolybdate,** $[Cu(NH_3)_4]MoO_4$, are formed. The crystals readily lose ammonia, and become dark green. S. H. C. Briggs prepared **copper diamminomolybdate,** $[Cu(NH_3)_2]MoO_4.H_2O$, by mixing a soln. of 24 grms. of pentahydrated copper sulphate in 30 c.c. of water, 13 grms. of ammonium paramolybdate in 15 c.c. of water, and 40 c.c. of conc. aq. ammonia, making all up to 350 c.c., and exposing it to air. The deep blue prisms lose ammonia at ordinary temp.; and they are soluble in warm aq. ammonia. The salt may be recrystallized by allowing the warm soln. in aq. ammonia to cool, or by exposing a more dil. ammoniacal soln. to air. H. Struve obtained **ammonium copper molybdate,** $(NH_4)_2O.CuO.5MoO_3.9H_2O$, from the mother-liquor of the oxymolybdate; and by the action of a cold soln. of copper sulphate on an excess of ammonium 2 : 5 : 3 molybdate. The pale blue, microscopic, rhombic crystals lose 4 mols. of water at 100°; more at a higher temp., and finally water and ammonia are given off. The yellow mass melts at a red-heat. It is sparingly soluble in cold water, and soluble in boiling water without decomposition. Blue crystals of **ammonium copper diamminomolybdate,** $(NH_4)_2Cu(MoO_4)_2.2NH_3$, were obtained by S. H. C. Briggs by exposing to air in an open dish a mixture of 50 grms. of ammonium molybdate in 60 c.c. of water, 20 grms. of ordinary copper sulphate in 50 c.c. of water, and 70 c.c. of conc. aq. ammonia, all made up to 210 c.c.

According to F. Wöhler and F. Rautenberg,[6] if normal silver molybdate be treated with hydrogen at ordinary temp., it is partially converted into **silver submolybdate,** $Ag_4O.2MoO_3$. It was also prepared by passing hydrogen into a soln. of silver molybdate in conc., aq. ammonia. The reduction begins at ordinary temp. as the liquid turns brown; the action is complete at 90°. The black powder consists of octahedral crystals belonging to the cubic system. The salt dissolves in nitric acid giving off nitric oxide; with potash-lye, molybdenum trioxide is dissolved, and silver suboxide is left as a black powder. W. Muthmann said that the alleged silver submolybdate is nothing more than a mixture of silver and the normal molybdate. C. W. Scheele, J. B. Richter, and L. F. Svanberg and H. Struve prepared **silver molybdate,** Ag_2MoO_4, as a white or yellowish-white, amorphous precipitate, by adding a silver salt to a soln. of a molybdate. E. F. Smith and R. H. Bradbury obtained it in a similar way. H. Debray obtained the salt in cubic crystals by allowing an ammoniacal soln. of ammonium molybdate and silver nitrate to evaporate spontaneously. W. Muthmann obtained the crystals in a similar way. R. W. G. Wyckoff studied the X-radiogram of the crystals, and showed that the structure is like that of the spinels or of magnetite. The length of the side of the unit cube, containing 8 mols., is 9·26 A. P. P. Ewald studied this subject. Silver molybdate is coloured when heated, and it readily melts to a yellow liquid. It forms a colloidal soln. with water, particularly when freshly precipitated; according to H. Rose, it readily dissolves in nitric acid; and, according to E. F. Smith and R. H. Bradbury, it dissolves in a soln. of potassium cyanide, or of sodium hydroxide. J. Krutwig observed that the fused salt is not attacked by chlorine; and O. Widman, that if the ammoniacal soln. is evaporated in an atm. of ammonia, or if the solid salt is treated with ammonia, **silver diamminomolybdate,** $[Ag(NH_3)_2]_2MoO_4$, is formed, in the latter case, as a white powder, and, in the former case, crystals which are probably isomorphous with the corresponding tungstate. The salt loses all its ammonia at 65°. P. Ray and J. Dasgupta prepared a complex with hexamethylenetetramine.

According to J. B. Richter,[7] when potassium molybdate is added to a soln.

of auric chloride, orpiment-yellow **gold molybdate** is precipitated. It is soluble in hydrochloric or nitric acid, and sparingly soluble in water.

W. H. Melville[8] described a greenish mineral which he obtained from the Seven Devils mining district, Idaho. It was named **powellite**—after J. W. Powell. It approximates in composition to normal **calcium molybdate,** $CaMoO_4$, associated with some calcium tungstate. F. Ullik obtained a white precipitate of calcium molybdate by adding calcium chloride to a soln. of neutral sodium molybdate. The precipitate does not form in cold, dil. soln., nor in the presence of acetic acid. The salt was obtained by E. F. Smith and R. H. Bradbury in a similar way. A. Kissock obtained it by treating roasted molybdenite with slaked lime; and H. C. Maber, by heating roasted molybdenite with calcium carbonate at 600°. F. de Carli observed that the reaction between calcium oxide and molybdenum trioxide begins at 650°. D. Balareff, W. Jander, and G. Tammann also studied this reaction. G. Tammann found the reaction between molybdenum trioxide and calcium oxide begins at about 425°; and with calcium carbonate above 600°. W. Jander studied the dynamics of the heterogeneous reaction $CaCO_3+MoO_3=CaMoO_4+CO_2$, between 487° and 550°, and examined the influence of the grain size of the component particles. H. Schultze, and L. Michel obtained crystals by melting a mixture of sodium molybdate, calcium chloride, and sodium chloride (1 : 3 : 2), and H. Traube obtained crystals as a sublimate when the molybdate is heated with a mixture of sodium and potassium chlorides to a high temp. According to T. H. Hiortdahl, the crystals are tetragonal bipyramids with the axial ratio $a:c=1:1\cdot5457$; and the sp. gr. is 4·35. From the X-radiograms, F. Zambonini and R. G. Levi gave for the dimensions of the unit cell $a=3\cdot67$ A., and $c=5\cdot69$ A., and they discussed the isomorphism of the molybdates of lead and the alkaline earth metals. E. Herlinger studied the structure of the crystals of the alkaline earth molybdates. A. Kissock discussed the use of calcium molybdate in steel making. Crystals of powellite were found by W. H. Melville to be tetragonal with the axial ratio $a:c=1:1\cdot5445$. F. Zambonini gave 1 : 5513—*vide infra,* the rare earth molybdates. W. Jander discussed the lattice-structure. L. Vegard and A. Refsum found that the X-radiogram of powellite corresponded with a space-lattice of the rutile type with $a_0=7\cdot4$ A., $c_0=11\cdot44$ A., and $a:c=1:1\cdot546$. The radius of the oxygen atom=1·12 A., that of the calcium atom, 1·03 A., and that of the positive ion, 1·12 A. The elementary cell has 8 mols. The sp. gr. is 4·526, and the hardness 3·5. F. Zambonini and R. G. Levi gave 4·28 for the sp. gr. P. P. Pilipenko gave 4·22 for the sp. gr. of some crystals from western Altai, and 3·5 to 4·0 for the hardness. F. Westphal studied the mixed crystals of calcium and ammonium molybdates. W. Jander studied the diffusion of the molybdate and tungstate. D. Balareff and N. Lukova found that calcium molybdate lowers the dissociation press. of calcium carbonate. E. Cane gave 0·166 for the sp. ht. G. Tammann gave for the heat of formation of $CaMoO_4$, 26·5 Cals. per mol. E. S. Larsen gave for the refractive indices of powellite, $Ca(Mo,W)O_4$, $\epsilon=1\cdot978$, and $\omega=1\cdot968$, or $\epsilon-\omega=0\cdot01$ for the D-line. F. Zambonini gave for $\lambda=667$, $\epsilon=1\cdot962$, $\omega=1\cdot959$, and $\epsilon-\omega=0\cdot008$; for $\lambda=570$, $\epsilon=1\cdot984$, $\omega=1\cdot974$, and $\epsilon-\omega=0\cdot010$; and for $\lambda=583$, $\epsilon=1\cdot993$, $\omega=1\cdot982$, and $\epsilon-\omega=0\cdot011$. H. Schultze obtained crystals of **strontium molybdate,** $SrMoO_4$, by fusing a mixture of sodium molybdate, strontium chloride, and sodium chloride (1 : 2 : 2). G. Tammann said that the reaction between molybdenum trioxide and strontium carbonate begins at about 700°. The tetragonal pyramids were found by T. H. Hiortdahl to have the axial ratio $a:c=1:1\cdot5738$. F. Zambonini and R. G. Levi gave for the dimensions of the unit cell $a=3\cdot79$ A., and $c=5\cdot97$ A., and they studied the isomorphism of the molybdates of lead and the alkaline earth metals. E. K. Brock gave $a=5\cdot380$ A., $c=11\cdot97$ A., $a:c=1:2\cdot226$; and the calculated density 4·718. W. Jander discussed the lattice-structure; and the diffusion of the molybdate and tungstate. F. W. Clarke gave 4·1554 for the sp. gr. at 20·5°, and 4·1348 at 21°; F. Zambonini and R. G. Levi gave 4·73; and V. G. Aranda, 4·6624. E. F. Smith and R. H. Bradbury found that 100 parts of water dissolve 0·0104 part of salt at 17°. F. Westphal studied the mixed crystals of strontium and ammonium molybdates. F. de Carli observed that the reaction between molybdenum trioxide and barium oxide begins at 290°. D. Balareff, J. H. Hevdall, and N. von Zweigbergh also studied this reaction. W. Jander represented the temp. coeff., k, of the reaction with calcium carbonate and molybdenum trioxide by $k=ce^{-43000/T}$, and the thermal value of the reaction by 21·5 Cals. E. Cane gave 0·149 for the sp. ht. L. F. Svanberg and H. Struve obtained **barium molybdate,** $BaMoO_4$, by adding barium chloride to a soln. of ammonium molybdate or paramolybdate in an excess of ammonia, and washing the product with cold water. H. Schultze obtained crystals by melting a mixture of sodium molybdate, barium chloride, and sodium chloride (1 : 3 : 2). G. Tammann said that the reaction between molybdenum trioxide and baryta begins at about 290° ; and with barium carbonate at 660°—W. Jander studied this reaction. The acicular crystals are tetragonal pyramids which, according to T. H. Hiortdahl, have the axial ratio $a : c=1 : 1·6232$. F. Zambonini and R. G. Levi gave for the dimensions of unit cell $a=3·96$ A., and $c=6·53$ A., and they studied the isomorphism of the molybdates of lead and the alkaline earth metals. L. Vegard and A. Refsum gave for the elementary cell, $a_0=7·858$ A., $c_0=12·755$ A., and $a : c=1 : 1·623$; the radius of the oxygen atom is 1·24 A. ; of the barium atom, 1·02 A. ; and of the positive ion, 1·21 A. W. Jander discussed the lattice-structure, and the diffusion of the molybdate and tungstate. F. W. Clarke gave 4·659 for the sp. gr. at 17·5°, and 4·648 at 19·5° ; F. Zambonini and R. G. Levi gave 4·84 ; and V. G. Aranda, 4·9747. E. Cane gave 0·113 for the sp. ht. G. Tammann gave 60·1 Cals. for the heat of formation of $BaMoO_4$. According to E. F. Smith and R. H. Bradbury, 100 parts of water at 23° dissolve 0·0058 part of the salt ; the solubility is augmented by the presence of ammonium nitrate. The salt is soluble in acids, and, when ammonia is added to the soln., C. J. Heine said that a basic salt is precipitated, but L. F. Svanberg and H. Struve found that the normal salt is so formed. L. Kahlenberg and W. J. Trautmann observed no reaction occurs when a mixture of barium molybdate and silicon is heated by the bunsen burner, but a slight reaction occurs in the electric arc.

A. Atterberg[9] found that if equimolar parts of beryllium hydroxide and molybdenum trioxide are boiled with water, for a long time, a voluminous precipitate consisting of interlaced needles of a basic salt—**beryllium oxymolybdate,** $BeO.BeMoO_3.3H_2O$—is formed. It loses a mol. of water at 100°. G. Tammann found that the reaction between molybdenum trioxide and beryllium oxide begins at about 400° ; and the heat of formation of **beryllium molybdate,** $BeMoO_4$, is 4·0 Cals. per mol. According to A. Rosenheim and P. Woge, the *dihydrate*, $BeMoO_4.2H_2O$, is obtained by boiling the theoretical quantity of hydrated beryllium oxide with molybdenum trioxide suspended in water. The oily liquid forms an aggregate of slender needles if kept for some time in the acid.

A. and E. Scacchi[10] obtained from an old rock embedded in Vesuvian lava, white needles consisting of tetragonal crystals of a mineral which they named **belonosite**—from βελόνη, a needle—and which was considered to be **magnesium molybdate,** $MgMoO_4$. F. de Carli observed no reaction between molybdenum trioxide and magnesia up to 1200°, but G. Tammann said that the reaction begins at about 425°, and the heat of formation of $MgMoO_4$ is 7·3 Cals. per mol. F. Ullik, M. Delafontaine, and H. Struve prepared the anhydrous salt by calcining, at not too high a temp., the hydrated salt obtained by boiling magnesia in water holding molybdenum trioxide in suspension, and evaporating the filtered liquid. G. N. Wyrouboff found that rhombic crystals of the *heptahydrate* are formed at about 30° ; and F. Westphal also obtained rhombic crystals of the heptahydrate which are isomorphous with heptahydrated magnesium sulphate ; and which lost five mols. of water at 80°. G. N. Wyrouboff observed that soln. at a temp. exceeding 30° yield the triclinic *pentahydrate.* The transition temp. has not been determined exactly. F. Westphal prepared the salt by mixing soln. of magnesium chloride and of sodium molybdate. A. and E. Scacchi described **belonosite** as a white mineral consisting of minute, acicular crystals of $MgMoO_4$, which are tetragonal with the axial ratio $a : c=1 : 0·66054$. W. Jander discussed the lattice-structure, and the diffusion of the molybdate and tungstate. The triclinic pentahydrate furnishes prismatic crystals isomorphous with the pentahydrates of copper sulphate, and magnesium sulphate and chromate. The axial ratios were found by G. N. Wyrouboff to be $a : b : c=0·5264 : 1 : 0·5732$, and $\alpha=80° 43'$, $\beta=98° 52'$, and $\gamma=107° 28'$. The sp. gr. is 2·208. Three mols. of water are lost at 120°, and the remainder at a red-heat without decomposing the molybdate. M. Delafontaine said that the salt is readily soluble in hot and cold water. F. Rodolico prepared a complex with hexamethylenetetramine, $MgMoO_4.X.10H_2O$.

F. Ullik prepared **ammonium magnesium molybdate,** $(NH_4)_2MoO_4.MgMoO_4.2H_2O$, by evaporating an equimolar soln. of the two salts spontaneously, or on a water-bath; and also by adding ammonia to a soln. of magnesium molybdate, and crystallizing the filtrate. V. von Zepharovich gave $a : b : c=0·851 : 1 : 0·436$ for the axial ratios of the probably rhombic, bipyramidal crystals. The (010)-cleavage is well defined; and the (100)-cleavage less so. When the salt is heated F. Ullik observed that water and ammonia are evolved; the salt is freely soluble in water. F. Ullik studied the isomorphism of the molybdates, sulphates, and chromates. If mixed soln. of magnesium molybdate and ammonium sulphate, or of magnesium sulphate and ammonium molybdate, are allowed to crystallize, isomorphous mixtures of the molybdato- and sulphato-complex salts are formed in which the ratio $MoO_3 : SO_3$ depends on the proportions of the radicles in the soln. With dil. soln. evaporated spontaneously, the salt which separates has a small proportion of molybdate, while a large proportion of molybdate is present if hot, sat. soln. are mixed. The crystals have the composition $(NH_4)_2Mg(MoO_4)_{2-n}(SO_4)_n.6H_2O$, and are monoclinic like the complex sulphates $(NH_4)_2Mg(SO_4)_2.6H_2O$. The mixed crystals were also studied by F. Westphal. F. Ullik also found that mixed soln. of magnesium molybdate and ammonium chromate also furnish isomorphous mixtures of the two salts. F. Ullik prepared crystals of **potassium magnesium molybdate,** $K_2Mg(MoO_4)_2.2H_2O$, by the method employed for the ammonium salt. The salt loses water and melts at a dull red-heat; and it is slowly dissolved by cold water, and quickly by hot water. F. Ullik found that mixed soln. of magnesium molybdate and potassium sulphate furnish crystals of the separate components, but with mixed soln. of molybdates and chromates, isomorphous mixtures of $K_2Mg(MoO_4)_{n-2}(CrO_4)_n.2H_2O$ are formed.

F. de Carli[11] observed that a reaction between molybdenum trioxide and zinc oxide begins at 270°. R. Brandes obtained a precipitate by adding ammonium molybdate to a soln. of a zinc salt, and the yellowish-white powder approximated in composition to **zinc molybdate,** $ZnMoO_4$. W. Jander discussed the lattice-structure; and the diffusion of the molybdate and tungstate. There is an interchange of acid radicle in the reactions $CdO+ZnMoO_4=CdMoO_4+ZnO$; $MgO+ZnMoO_4=MgMoO_4+ZnO$; $MgO+CdMoO_4=CdO+MgMoO_4$; and $MgO+MnMoO_4=MgMoO_4+MnO$. R. Brandes said that zinc molybdate is sparingly soluble in water; and readily soluble in acids. A. Coloriano, and E. Manassewitsch showed that the product obtained by precipitation is really the *monohydrate,* which does not lose all its water at 100°. H. Schultze obtained minute needles of the anhydrous salt by fusing together a mixture of sodium molybdate, zinc chloride, and sodium chloride (2 : 3 : 6), and washing the cold mass with water. The salt is fusible. F. L. Sonnenschein prepared crystals of **zinc diamminomolybdate,** $Zn(NH_3)_2MoO_4.H_2O$, by evaporating the filtered liquid obtained by digesting zinc oxide with an ammoniacal soln. of ammonium molybdate.

F. de Carli observed that a reaction between cadmium oxide and molybdenum trioxide begins at about 500°. R. Brandes obtained what appears to have been **cadmium molybdate,** $CdMoO_4$, by precipitation as in the case of the analogous zinc salt; and H. Schultze obtained yellow plates of the anhydrous salt by melting together sodium molybdate, cadmium chloride, and sodium chloride (2 : 7 : 6).

The salt was also obtained by the precipitation process by E. F. Smith and R. H. Bradbury, A. Junius, and E. Manassewitsch. E. K. Broch calculated from the X-radiograms, the space-lattice with a=5·138 A., c=11·17 A., $a:c$=1 : 2·174; and the density, 5·347. W. Jander studied the diffusion of the molybdate and tungstate. The salt is sparingly soluble in water, freely soluble in acids, aq. ammonia, and soln. of potassium cyanide. S. H. C. Briggs obtained colourless crystals of **ammonium cadmium diamminomolybdate,** $(NH_4)_2CdMoO_4(NH_3)_2$, from an ammoniacal soln. of cadmium sulphate and ammonium molybdate as in the case of the corresponding copper salt. The salt is partially decomposed when heated.

H. Struve[12] treated potassium trimolybdate with mercurous nitrate and washed the resulting dimolybdate with water until it formed golden-yellow needles of **mercurous molybdate,** Hg_2MoO_4; the change occurs more rapidly if the precipitate and mother-liquor be boiled for a long time. C. W. Scheele said that mercuric chloride does not give a precipitate with molybdic acid; but J. J. Berzelius, and C. Hatchett observed that with potassium molybdate a yellow precipitate of **mercuric molybdate** is produced which is decomposed by nitric acid; 100 parts of water dissolve 0·167 to 0·200 part of the salt. According to C. H. Hirzel, finely-divided mercuric oxide is rapidly attacked by a conc. soln. of acid ammonium molybdate, and after boiling for some hours, a yellowish-white, granular precipitate is formed—no ammonia is given off, and no mercury passes into soln. The composition of the precipitate was not determined.

H. Struve,[13] and J. G. Gentele were unable to prepare normal **aluminium molybdate;** nor has **gallium molybdate** been obtained. The aluminium molybdates are discussed below. G. Tammann observed no reaction between alumina and molybdenum trioxide below 700°. C. Renz prepared **indium molybdate,** $In_2(MoO_4)_3.2H_2O$, by the action of ammonium molybdate on a soln. of an indium salt; the white precipitate dries to a horn-like mass; it is insoluble in water, and soluble in hydrochloric acid. M. Delafontaine prepared **thallous molybdate,** Tl_2MoO_4, by boiling thallous oxide or carbonate with water and molybdic acid; P. S. Oettinger, and H. Fleming, by double decomposition of a soln. of a thallous salt with a normal molybdate; and F. Mauro, by roasting thallous molybdenum dioxytetrafluoride at a red-heat in air. It separates from a hot aq. soln. as a crystalline powder, or in tabular crystals. It melts at a red-heat to form a yellow liquid, and partial volatilization occurs. The salt is soluble in alkali-lye; and it dissolves in hydrofluoric acid to form a soln. which when evaporated over sulphuric acid, furnishes crystals of thallous molybdenum dioxytetrafluoride.

P. Didier[14] prepared **cerous molybdate,** $Ce_2(MoO_4)_3$, by fusing a mixture of anhydrous cerous chloride and sodium molybdate; and A. Cossa observed that a soln. of a cerous salt gives a gelatinous white precipitate when treated with sodium molybdate; the precipitate becomes yellow and crystalline. H. Traube obtained crystals of cerium molybdate as a sublimate by the method indicated in connection with calcium molybdate. G. Tammann said that the reaction between cerium dioxide, and molybdenum trioxide begins at about 650°, and $Ce_2(MoO_4)_3$ is formed. The sp. gr. of the salt, which has been fused in an inert atm., is 4·56. F. Zambonini and R. G. Levi gave 5·03 for the sp. gr. According to A. Cossa, the crystals are tetragonal and are isomorphous with wulfenite; they have the axial ratios $a:c$=1 : 1·558. F. Zambonini found that the air-dried precipitate is the trihydrate, $Ce_2(MoO_4)_3.3H_2O$. He obtained crystals of the anhydrous salt by fusing the precipitated salt in an electric furnace, and slowly cooling the mass; he gave for the axial ratio of the rhombic crystals $a:b:c$=0·6631 : 1 : 0·8212. The sp. gr. of the rhombic crystals is 4·83 at 20°/20°; the mol. vol., 167·4; and the m.p., 930°. F. Zambonini also obtained a tetragonal form by heating the salt dried at 180° to 1050° and slowly cooling it from 900°—the axial ratio was $a:c$=1 : 1·5624; F. Zambonini and R. G. Levi gave for the dimensions of unit cell a=3·77 A., and c=5·81 A. F. Zambonini gave 5·03 for the sp. gr. at 18°/18°; and for the mol. vol., 151·2.

E. Cane gave 0·126 for the sp. ht. The indices of refraction and dispersions for $\lambda=667$, 570, and 533 are respectively $\omega=2·0185$, $\epsilon=2·0067$, and $\omega-\epsilon=0·0118$; $\omega=2·0403$, $\epsilon=2·0277$, and $\omega-\epsilon=0·0126$; and $\omega=2·0512$, $\epsilon=2·0375$, and $\omega-\epsilon=0·0137$. S. Prakash and N. R. Dhar obtained the hydrogel of ceric molybdate. The crystal plates obtained in preparing the tetragonal form appear to be **cerous ceric** or **cerosic molybdate,** $Ce_2(MoO_4)_3.2Ce(MoO_4)_2$. E. Herlinger studied the crystal structure. F. Zambonini prepared isomorphous mixtures of tetragonal crystals of calcium and cerous molybdates containing up to 59·1 per cent. of cerous molybdate. The axial ratios $a:c$ of the tetragonal crystals with 0, 6·5, and 59·1 per cent. of cerous molybdate are, respectively, 1 : 1·5513, 1 : 1·5492, and 1 : 1·5510. Isomorphous mixtures of crystals of cerous and strontium molybdates with up to 39·7 per cent. of the cerium salt were prepared. The refractive indices for light of wave-length λ were:

	2·4 per cent. $Ce_2(MoO_4)_3$.			39·7 per cent. $Ce_2(MoO_4)_3$.		
λ	ϵ	ω	$\epsilon-\omega$	ϵ	ω	$\epsilon-\omega$
667 . .	1·9127	1·9088	0·0039	1·940	1·937	0·003
570 . .	1·9258	1·9210	0·0048	1·956	1·952	0·004
533 . .	1·9350	1·9290	0·0060	1·963	1·958	0·005

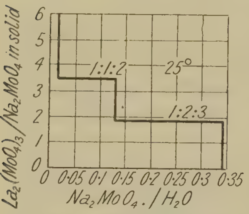


FIG. 22.—Equilibrium in the System: $La_2(MoO_4)_3$–Na_2MoO_4–H_2O.

F. T. Frerichs and E. F. Smith prepared **lanthanum trihydromolybdate,** $LaH_3(MoO_4)_3$, as a precipitate by adding ammonium molybdate to a lanthanum salt. F. R. M. Hitchcock obtained the normal **lanthanum molybdate,** $La_2(MoO_4)_3$, by adding sodium molybdate to a soln. of lanthanum chloride, and dehydrating the gelatinous precipitate. H. Traube obtained crystals as a sublimate by the method indicated for calcium molybdate. F. Zambonini fused the salt and by slow cooling obtained tetragonal, bipyramidal crystals with the axial ratio $a:c=1:1·5504$. F. Zambonini and R. G. Levi gave for the dimensions of the elementary cell, $a=3·78$ A. and $c=5·68$ A. F. Zambonini found that the optical character was negative. The sp. gr. is 4·77 at 16°/16°; the mol. vol., 158·9; and the m.p., 1181°. E. Cane gave 0·114 for the sp. ht. G. Carobbi's study of the ternary system: $La_2(MoO_4)_3$–Na_2MoO_4–H_2O at 25°, and the results, Fig. 22, show the existence of the two **sodium lanthanum molybdates:** $La_2(MoO_4)_3.Na_2MoO_4.2H_2O$, and $La_2(MoO_4)_3.2Na_2MoO_4.3H_2O$. F. Zambonini found that isomorphous mixtures were obtained with lead molybdate (*q.v.*), with up to 42 per cent. of calcium molybdate; with up to 62·5 per cent. of strontium molybdate; and with up to 86·9 per cent. of barium molybdate. F. T. Frerichs and E. F. Smith obtained **didymium trihydromolybdate,** $DiH_3(MoO_4)_3$ as in the case of the lanthanum salt. A. Cossa also prepared didymium molybdate, $Di_2(MoO_4)_3$. H. Traube obtained crystals as a sublimate by the method indicated for calcium molybdate in tetragonal crystals, which, according to F. Zambonini have the axial ratio $a:c=1:1·5489$. The sp. gr. is 4·96 at 16·5°/16·5°. The m.p. is 1125°, but it is not sharp. The double refraction is negative, and there are no optical anomalies. The index of refraction is 2·008 for the *B*-line; 2·012 for the *C*-line; 2·026 for the *D*-line; 2·039 for the *E*-line; and 2·054 for the *F*-line. Isomorphous mixtures were obtained with lead molybdate (*q.v.*), and with calcium molybdate. The crystals with about 61·2 per cent. of calcium molybdate have a feebly positive birefringence. The indices of refraction for light of wave-length λ are:

λ . .	667	599	570	533	475
ϵ . .	1·9869	1·9947	2·0020	2·0094	2·0212
ω . .	1·9902	1·0089	2·0068	2·0139	2·0258
$\epsilon-\omega$ . .	0·0033	0·0042	0·0048	0·0045	0·0046

F. R. M. Hitchcock prepared **neodymium molybdate,** $Nd_2(MoO_4)_3$; and F. Zambonini found that the air-dried substance has the composition $Nd_2(MoO_4)_3.4H_2O$. When heated with molten sodium chloride, violet crystals are formed. The axial ratio of the tetragonal crystals is $a:c=1:1·5480$. F. Zambonini and R. G. Levi gave for the dimensions of the elementary cell $a=3·74$ A., and $c=5·79$ A. F. Zambonini found that the birefringence is negative; the indices of refraction and dispersions for $\lambda=667$, 570, and 533 are respectively $\omega=2·0052$, $\epsilon=2·0038$, and $\omega-\epsilon=0·0014$; $\omega=2·0239$, $\epsilon=2·0218$, and $\omega-\epsilon=0·0021$; and $\omega=2·0313$, $\epsilon=2·0293$, and $\omega-\epsilon=0·0020$. The sp. gr. is 5·14 at 18°/18°; the mol. vol., 149·5; and the m.p., 1176°—*vide infra*, lead molybdate. F. R. M. Hitchcock prepared **praseodymium molybdate** by precipitation with praseodymium chloride and sodium molybdate soln. F. Zambonini found that when dried over sulphuric acid, the gelatinous precipitate has the composition $Pr_2(MoO_4)_3.3\frac{1}{2}H_2O$; and when heated with fused sodium chloride, the anhydrous salt furnishes tetragonal bipyramids with the axial ratio $a:c=1:1·5439$. F. Zambonini and R. G. Levi gave for the dimensions of the elementary cell, $a=3·76$ A., and $c=5·805$ A. F. Zambonini found that the sp. gr. is 4·84 at 16·5°/16·5°; the mol. vol. is 157·3; and the m.p., 1030°. The birefringence is negative; and the index of refraction $\epsilon=1·990$, 2·007, and 2·016 respectively for $\lambda=667$, 570, and 533. P. T. Cleve obtained **samarium molybdate,** $Sm_2(MoO_4)_3$, in violet, rhombic octahedra, by calcining a mixture of samarium oxalate, sodium chloride, and molybdenum trioxide. F. Zambonini and R. G. Levi found the dimensions of the unit cell to be $a=3·69$ A., and $c=5·81$ A., the axial ratio $a:c=1:1·5745$. The sp. gr. is 5·36. A. Cleve prepared **sodium samarium molybdate,** $SmNa(MoO_4)_2$, in pale red needles. The two salts can be separated by levigation in water. F. Zambonini prepared **yttrium molybdate,** $Y_2(MoO_4)_3.4H_2O$, by drying over calcium chloride the precipitate obtained by adding a soln. of sodium molybdate to one of yttrium nitrate. When melted, and slowly cooled, it furnishes greyish-white or yellow crystal plates which belong to the tetragonal system, and have the axial ratio $a:c=1:1·5422$; the (001)-cleavage is incomplete; the sp. gr. is 4·79 at 16°/16°; the mol. vol. is 137·4; the m.p. is 1347°; and the index of refraction, ϵ, for $\lambda=667$ is 2·013; for $\lambda=570$, 2·031; and for $\lambda=533$, 2·043. Isomorphous mixtures with lead molybdate (*q.v.*), and with calcium molybdate were prepared. E. Cane gave 0·159 for the sp. ht., F. Zambonini found that the crystals with 95·3 per cent. of the calcium salt had the respective indices of refraction and dispersions $\epsilon=1·986$, $\omega=1·978$, and $\epsilon-\omega=0·008$ for $\lambda=667$; $\epsilon=2·002$, $\omega=1·998$, and $\epsilon-\omega=0·004$ for $\lambda=570$; and $\epsilon=2·012$, $\omega=2·003$, and $\epsilon-\omega=0·009$ for $\lambda=533$. It was found that the presence of cerous molybdate favours the formation of isomorphous mixtures with higher proportions of calcium. Crystals containing 24·7 per cent. of yttrium molybdate, 21 per cent. of cerous molybdate and 44·3 per cent. of calcium molybdate had the axial ratio $a:c=1:1·5436$, a positive birefringence, and the indices of refraction for the *C*-, *D*-, and *E*-lines respectively $\epsilon=1·9939$, 2·0049, and 2·0208; $\omega=1·9905$, 2·0004, and 2·0163; and $\epsilon-\omega=0·0034$, 0·0045, and 0·0045. A. Cleve obtained **ytterbium oxymolybdate,** $Yb_2O_3.Yb_2O_2(MoO_4)$, as a green crystalline powder, by heating ytterbium oxide, molybdenum trioxide, and sodium chloride at a high temp.

The **silicon molybdates,** or **silicomolybdates,** were discussed in connection with the silicates—**6**. 40, 50. For the **titanium molybdates,** *vide infra.* O. Kulka[15] treated a cold, aq. soln. of ammonium paramolybdate with zirconium sulphate, and obtained a slimy precipitate which, when washed with hot water, approximated to **zirconium molybdate,** $Zr(MoO_4)_2.21H_2O$. It is insoluble in water, but soluble in hot, conc. hydrochloric acid. Zirconium hydroxide is insoluble in an aq. soln. of alkali molybdate. S. Prakash and N. R. Dhar obtained the hydrogel of zirconium molybdate. S. M. Tanatar and E. K. Kurowsky prepared **zirconium oxychloromolybdate,** $ZrCl_4.mZr_3(MoO_4)_2.nZrO_2$. J. J. Berzelius obtained **thorium molybdate** as a white precipitate by adding a soln. of an alkali molybdate to one of a thorium salt; and J. J. Chydenius, by mixing a feebly acid soln. of thorium tetrachloride with an ammoniacal soln. of ammonium molybdate. F. Zambonini obtained the anhydrous salt, $Th(MoO_4)_2$, by fusing partly-dehydrated thorium chloride with an excess of anhydrous sodium molybdate. The tetragonal crystals have the axial ratio $a : c = 1 : 0{\cdot}73565$; and the sp. gr. 4·92 at 7·5°/7·5°. They form isomorphous mixtures with those of cerous molybdate. S. Prakash and N. R. Dhar prepared the hydrogel of thorium molybdate.

The blue colour obtained by J. B. Richter[16] by mixing an alkali molybdate with stannous chloride, or by the action of tin and hydrochloric acid on molybdenum trioxide suspended in water was shown by J. J. Berzelius to be a mixture of stannic molybdate and a blue lower oxide of molybdenum. H. Schiff said that the blue pigment contains no tin, and, according to G. Denigès, it is produced by other reducing agents. J. P. Longstaff recommended the reaction as a test for tin. F. de Carli observed that a reaction between stannous oxide and molybdenum trioxide begins at 400°. J. J. Berzelius obtained **stannic molybdate,** as a grey powder insoluble in water, and soluble in hydrochloric acid with a blue or green coloration; and in potash-lye with a brown coloration. It is not decomposed by nitric acid. S. Prakash and N. R. Dhar dialyzed for 2 days a mixture of $1{\cdot}5M$-$SnCl_2$ with a 25 per cent. soln. of potassium molybdate. The clear soln. was mixed with an equal vol. of water. It set to a jelly in 5 hrs. The viscosities at 30° were:

Age .	0	3	5	10	20	30	40	60	80 min.
Viscosity	0·01272	0·01353	0·01471	0·01804	0·02300	0·03032	0·03447	0·04412	0·07505

I. Eques a Born[17] described a mineral *plumbum spatosum flavorubrum* from Annaberg, and it was also examined by N. J. von Jacquin, and F. X. Wulfen. J. B. L. Romé de l'Isle called it *plomb jaune;* A. G. Werner, *Gelbbleierz;* R. Kirwan, *yellow lead-spar* or *molybdenated lead ore;* F. S. Beudant, *melinose;* and W. Haidinger, **wulfenite**—after F. X. Wulfen. Analyses were reported by J. C. H. Heyer, M. H. Klaproth, C. Hatchett, F. Göbel, I. Domeyko, F. Jost, J. L. Smith, F. Reinitzer, C. L. Allen, C. Schmidt, C. F. Rammelsberg, G. Rose, J. F. W. Johnston, K. Schlier, V. von Zepharovich, A. Schrauf, H. Regnard, and F. Wöhler. The mineral approximates in composition to **lead molybdate,** $PbMoO_4$. The lead may be partly replaced by lime forming, according to I. Domeyko, and V. von Zepharovich, *calcium lead molybdate*, or else an isomorphous mixture. Specimens from Pribram were found by P. Groth to contain chromium—*chromowulfenite*—similarly, A. Schrauf, J. L. Smith, and G. Rose found chromium in specimens from Ruksberg, Phœnixville, etc.; and E. F. Smith, C. F. Rammelsberg, and F. Wöhler reported samples with vanadium; G. Carobbi, samples with rare earths; and H. Regnard, samples with arsenic. The mineral occurs in nature associated with other lead ores at Lackentyre, Scotland; Chalanches, and Beaujolais, France; Gorno, Italy; Sarrabus, and Gennamari, Sardinia; St. Luc, Switzerland; Bleiberg, Carinthia; Ruskitza, Austria; Rezbanya and Szaska, Hungary; Pribram, Czechoslovakia; Moldawa, Banat; Annaberg, Schneeberg, Johanngeorgenstadt, and Berggieshübel, Saxony; Badenweiler, Baden; Kirghiz Steppes, Siberia; Mindouli, French Congo; in Massachusetts, Arizona, New York, Pennsylvania, Nevada, New Mexico, and California, United States; Rio Chico, Colombia; Zacatecas, Mexico, etc. The mode of formation of wulfenite was discussed by E. Dittler, G. Bischof, A. Himmelbauer, M. Henglein, C. Schmidt, G. Cesaro, and A. W. Stelzner-Bergeat. J. F. L. Hausmann observed it as a furnace product.

F. de Carli observed that a reaction between molybdenum trioxide and lead oxide begins at 650°; W. Jander said 450°; and G. Tammann, and J. Guillissen, 460°. D. Balareff said that the maximum effect occurs at 700°. J. J. Berzelius prepared lead molybdate by mixing soln. of lead nitrate or acetate and ammonium molybdate; G. Wempe, and H. B. Weiser used acid ammonium molybdates; and L. F. Svanberg and H. Struve, T. M. Chatard, E. F. Smith and R. H. Bradbury, A. Junius, H. B. Weiser, F. M. Jäger and H. C. Germs used sodium molybdates. E. Dittler treated white-lead with a soln. of sodium hydroxide containing 6 per cent. of ammonium 5 : 12-molybdate for 90 days on a water-bath in an atm. of carbon dioxide, and washed out the carbonate with very dil. hydrochloric acid. N. S. Manross melted a mixture of sodium molybdate and lead chloride (1 : 6) in a closed crucible. F. Zambonini used a similar process. H. Traube obtained crystals as a sublimate by the method used for calcium molybdate. H. B. Weiser obtained **colloidal lead molybdate** by precipitation and washing with hot water. The colloid is peptized by the selective adsorption of molybdate ions. N. R. Dhar and S. Ghosh found that lead molybdate is peptized by ammonium molybdate. The salt was analyzed by J. J. Berzelius, L. F. Svanberg and H. Struve, N. S. Manross, E. Dittler, A. Junius, G. Wempe, and H. C. Germs, and the results agree with the formula $PbMoO_4$.

The precipitated salt is a white, or yellowish-white powder, it also appears in yellowish-white, six-sided plates, octahedra, and pyramids. The colour of wulfenite may be wax-yellow passing into orange-yellow, orange, siskin-green or olive-green, yellowish-grey; greyish-white, or almost white, brown, or bright red. J. L. Smith said the red colour is due to vanadates; G. Rose, to chromium; P. Groth, to organic matter; and E. Dittler, to colloidal molybdic oxide. M. Bamberger and R. Grengg said that the colour of the natural crystals is white at —190°. E. Dittler observed no change in colour occurs when red wulfenite is heated to 700° in a current of air; and if the finest powder of brownish-yellow wulfenite is heated to 80°, it becomes lemon-yellow. A. Coloriano converted the amorphous powder into crystals by a prolonged digestion with water; and A. Cossa said that the fused salt furnishes microscopic, doubly-refracting pyramids. Wulfenite may occur in fine or coarse granular masses, in compact masses, and in square plates sometimes extremely thin with a vicinal pyramid replacing the basal plane. The crystals are less frequently octahedral or prismatic. The prismatic faces show the characteristic hemihedrism. H. Dauber said that the crystals of wulfenite are tetragonal pyramids with the axial ratios $a : c$ =1 : 1·577; T. H. Hiortdahl gave 1 : 1·5771; L. Bach, 1 : 1·5774; E. Flint, 1 : 1·5746; and V. von Zepharovich gave 1 : 1·5744 for a calcareous variety. The (111)-cleavage is incomplete; and the (001)- and (113)-cleavages are indistinct. The crystals were examined by A. Damour and A. des Cloizeaux, V. von Zepharovich, E. Hunek, F. N. Guild and F. S. Wartmann, L. J. Spencer, P. Groth, S. Koch, E. Flint, P. Comucci, A. Maier, J. Couyat, N. von Kokscharoff, E. Artini, L. Fletcher, A. Pelloux, A. Lacroix, E. Repossi, A. Drain, O. G. Padurova, and A. Sigmund. The percussion figures were examined by M. Kuhara; and the corrosion figures, by A. P. Honess; R. G. Dickinson inferred from the X-radiograms that the space-lattice is face-centred with the atoms so located as to form a diamond arrangement, Fig. 23—the sp. gr. is 6·82, and the edge of unit cube with 8 mols. is a=22·8 A. F. Zambonini and R. G. Levi found for the dimensions of the elementary cell, a=3·80 A., and c=6·00 A., and they studied the isomorphism of the molybdates of lead and the alkaline earth metals. F. M. Jäger and H. Haga attributed the high symmetry shown by the X-radiograms of wulfenite to twinning. L. Vegard and A. Refsum gave a_0=7·656 A., c_0=12·079 A., and $a : c$=1 : 1·578; the radius of the oxygen atom is 1·18 A., of the lead atom, 1·03 A., and of the positive ion, 1·17 A. M. L. Huggins discussed the structure of the crystals. D. Vorländer and H. Hempel observed no transformation into an isotropic form with rise of temp. The sp. gr. of wulfenite ranges from 6·03 to 7·01. C. L. Allen gave 6·7 at 17·5°; and J. L. Smith, 6·95; A. Cossa gave for the artificial crystals 6·62; F. Zambonini and R. G. Levi, 6·95; V. G. Aranda, 6·6933; and N. S. Manross, 6·811.

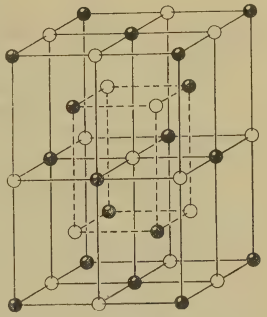


Fig. 23.—Arrangement of Atoms in Lead Molybdate: ● represents lead atom, and ○ a molybdenum atom.

J. J. Saslawsky found that the sp. gr. of wulfenite corresponds with a contraction of 0·60 to 0·68 during its formation from its elements. The hardness of wulfenite is 2·75 to 3·0. E. Jannetaz found the ratio of the heat conductivities of the crystals, α/γ, to be unity. H. Kopp gave for the mol. sp. ht. of wulfenite from Bleiberg, 0·0287 between 19° and 50°. E. Dittler observed that the m.p. in an atm. of carbon dioxide is 1070° and the optical properties of the cold mass are the same as before fusion. F. M. Jäger and H. C. Germs said that wulfenite from Arizona melts at 1064°, from La Cruces, Mexico, at 1060°; and artificial lead molybdate at 1065°. F. Zambonini gave 1065° for m.p.; the latent heat is said to be small, and the undercooling not more than 2°. E. Cane gave 0·098 for the sp. ht. G. Tammann gave 33·1 Cals. for the heat of formation of $PbMoO_4$. L. J. Spencer gave for the indices of refraction, $\omega=2{\cdot}41$, and $\epsilon=2{\cdot}32$ for yellow light. W. Schneider observed no piezoelectric effect. T. W. Case observed no electrical conductivity with wulfenite in light or in darkness. E. E. Fairbanks gave 11·7 for the dielectric constant (water 81). They found that the thermal diagram of the system: PbO–$PbMoO_4$, Fig. 24, shows only two compounds, the normal molybdate melting at 1065°; and the basic salt or **lead oxymolybdate,** $Pb_2O(MoO_4)$, melting at 951°. There are two eutectics: one at 762° corresponding with 87·5 molar per cent. PbO, and the other at 933° corresponding with 40 molar per cent. PbO. In the system: $PbSO_4$–$PbMoO_4$, Fig. 25, solid soln. are formed containing up to 6 molar per cent. of sulphate or 2 molar per cent. of molybdate. There is a eutectic at 962° and 57 molar per cent. PbO; and a transition point in the solid soln. at 879°. The thermal diagram of the system: $PbCrO_4$–$PbMoO_4$, Fig. 26, is largely hypothetical. The composition of the limiting solid soln. on the molybdate side is 48 molar per cent. $PbCrO_4$ at 830°, the eutectic temp.; and transitions occur at 799° for the γ- to β-chromate, and at 697° for the β to α-chromate solid soln. H. Schultze also obtained tetragonal isomorphous mixtures with up to 34 per cent. of lead chromate, and monoclinic mixed crystals with up to 16 per cent. The mineral *achrematite*, or *lead oxymolybdatochloroarsenate*, $3\{3Pb_3(AsO_4)_2.PbCl_2\}.4Pb_2MoO_5$, was discussed in connection with the arsenates.

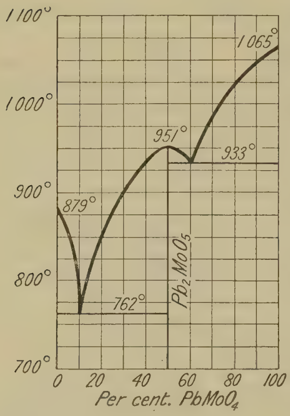


Fig. 24.—Freezing-point Curve in System: $PbMoO_4$–PbO.

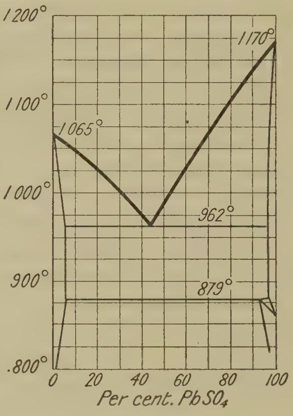


Fig. 25.—Freezing-point Curve in System: $PbMoO_4$–$PbSO_4$.

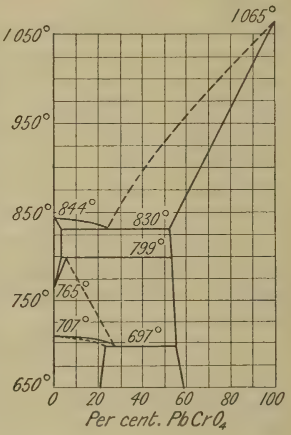


Fig. 26.—Freezing-point Curve in System: $PbMoO_4$–$PbCrO_4$.

P. Ites gave for the extinction coeff. of wulfenite for the *C*-, *D*-, and *E*-rays, respectively, 0·0486, 0·0625, and 0·455; and the indices of refraction $\omega=2{\cdot}4053$, and $\epsilon=2{\cdot}283$. According to A. des Cloizeaux, the optical character of wulfenite is negative; and the indices of refraction are $\omega=2{\cdot}402$, and $\epsilon=2{\cdot}304$ for red light.

H. C. Sorby found the mean refractive index to be 2·370, and the refractory power 0·682. A. Pochettino studied the cathodic luminescence; E. Dittler found that ultra-violet light makes the colour of chromiferous wulfenite darker; and C. Doelter observed that no change in colour occurs with radium rays. L. Francesconi and co-workers found that wulfenite from Sardinia is radioactive. R. Pohl found that when exposed to light, wulfenite becomes electrically conducting.

E. Dittler found that water at 100° very slowly dissolves colloidal molybdic acid from wulfenite—in 120 hrs. in an extraction apparatus about 5 per cent. was dissolved—no lead passed into soln. J. J. Berzelius said that alkali-lye dissolves wulfenite, but E. Dittler added that 0·1N-KOH has no action, but with a conc. soln. of the alkali, hexagonal crystals of *potassium lead molybdate* are formed. C. Bärwald obtained a complex $14NH_3.18MoO_3.3H_2O_2.18H_2O$, by the action of ammonia and hydrogen dioxide on lead molybdate. As indicated above, *calcium lead molybdate* is represented by the isomorphous mixtures in some specimens of wulfenite. J. J. Berzelius observed that conc. hydrochloric acid dissolves wulfenite, forming a soln. of lead chloride. E. Dittler, and W. Meyerhoffer said that an excess of fused sodium chloride does not convert wulfenite into sodium molybdate and lead chloride; and E. Dittler observed no action by a soln. of sodium chloride at 100°. The solubility of lead molybdate, S grms. per 100 c.c., in perchloric acid at 25°, was found by H. H. Willard and J. L. Kassner to be:

$HClO_4$	0·1M-	0·50M-	1·0M-	2·0M-	3·0M-
S.	0·0016	0·0136	0·0373	0·1176	0·2436

The effect of the presence of sodium or lead perchlorate is to depress the solubility. E. Dittler found that hydrogen sulphide colours wulfenite brown in a few minutes; and in about 12 hrs. the powdered mineral suspended in water is completely converted by hydrogen sulphide into molybdenum and lead sulphides; A. Terreil found that a boiling 10 per cent. aq. soln. of sodium sulphide decomposes wulfenite forming a liquid containing thiosulphate and molybdenum. E. F. Smith noted that heated sulphur monochloride dissolves wulfenite. J. J. Berzelius said that wulfenite is decomposed by sulphuric acid; and that treatment with warm nitric acid results in the separation of yellowish-white molybdenum trioxide. H. B. Weiser found that a hot aq. soln. of ammonium nitrate has no solvent action. H. H. Willard and J. L. Kassner found that the solubility of lead molybdate in 0·10M-, 0·50M-, and 1·0M-HNO_3 at 25° is 0·0020, 0·0244, and 0·1086 grm. per 100 c.c. respectively; the effect of lead or sodium nitrate is to depress the solubility. According to E. Dittler, water containing carbon dioxide has very little action in the cold, but at 100°, the mineral is decomposed and 3·66 per cent. passes into soln. A soln. of sodium carbonate, heated for 6 days on a water-bath, decomposes wulfenite, forming $Pb_3(OH)_2(CO_3)_2$, and some lead and molybdenum pass into soln. H. B. Weiser said that acetic acid does not dissolve freshly-precipitated lead molybdate, but soln. of ammonium or sodium acetate dissolve a little. H. C. Bolton observed that a boiling conc. soln. of citric acid decomposes wulfenite. L. Kahlenberg and W. J. Trautmann observed no reaction occurs when a mixture of silicon and lead molybdate is heated by a bunsen burner, but a slight reaction occurs in the electric arc. F. Zambonini prepared isomorphous mixtures of lead and cerous molybdates. The thermal analysis shows the following f.p.:

$Ce_2(MoO_4)_3$	0	20	30	50	70	90	95	100 per cent.
Beginning	1065°	1074°	1064°	1050°	1024°	975°	938°	973°
End .	—	—	—	1025°	1000°	—	—	—

The eutectic temp. is 938° with 95 per cent. of cerous salt. Some optical observations were made on the products. For isomorphous mixtures of lead molybdate with molybdates of lanthanum, neodymium, praseodymium, didymium, and yttrium, F. Zambonini found:

Rare earth salt		0	20	40	60	80	100 per cent.
La	Beginning	1065°	1085°	1109°	1139°	1163°	1181°
	End	—	1078°	1102°	1134°	1156°	—
Nd	Beginning	1065°	1076°	1088°	1115°	1147°	1176°
	End	—	1070°	1080°	1105°	1135°	—
Pr	Beginning	1065°	1072°	1068°	1054°	1043°	1030°
	End	—	1068°	1064°	1050°	1040°	—
Di	Beginning	1065°	1072°	1079°	1106°	1123°	1144°
	End	—	1067°	1075°	1085°	1100°	—
Sm	Beginning	1065°	1038°	1016°	1038°	1235°	1347°
	End	—	977°	976°	974°	974°	—

The **arsenic molybdates** were discussed in connection with arsenic—**9**. 51, 22; and the **antimony molybdates,** in connection with antimony—**9**. 52, 14. According to J. B. Richter,[18] when a soln. of bismuth nitrate is treated with potassium molybdate, a lemon-yellow precipitate of **bismuth molybdate,** presumably $Bi_2(MoO_4)_3$, is formed which is easily soluble in the strong acids; whilst 100 parts of water dissolve 0·2 part of the precipitate. By fusing an intimate mixture of bismuth and molybdenum trioxides, F. Zambonini obtained the salt in tetragonal crystals with the axial ratio $a:c=1:1·5636$, and sp. gr. 6·07 at 15°/15°. The mol. vol. is close to those of the molybdates of lead and the cerium metals. The m.p. is 643°. W. T. Schaller obtained greenish rectangular crystals of a mineral from Schneeberg, Saxony; he called it **koechlinite**—after R. Koechlin—and found the analysis corresponds with **bismuth dioxymolybdate,** $Bi_2O_3.MoO_3$, or **bismuthyl molybdate,** $(BiO)_2MoO_4$. The habit of the crystals is tabular, but the thin tablets vary in shape from square to elongated rectangles with diagonal striations. The axial ratios of the rhombic crystals are $a:b:c=0·9774:1:1·0026$. The (100)-cleavage is perfect. Both contact and penetration twinning occurs. The corrosion figures with cold dil. hydrochloric acid (1 : 5) suggested a deviation from holohedral symmetry. The crystals break readily under a slight press. The index of refraction is $\beta=2·55$ with Li-light. The crystals are slightly pleochroic when thick. E. F. Smith and R. H. Bradbury said that the bismuth salt is insoluble in water. Bismuth can be quantitatively precipitated as **ammonium bismuth molybdate,** $Bi(NH_4)(MoO_4)_2$, from a soln. of bismuth nitrate, feebly acid with nitric acid, by means of ammonium molybdate. Thus, E. H. Miller and F. van Dyke Cruser said that the nitric acid soln. of the bismuth is mixed with a large excess of the ordinary ammonium molybdate reagent and the liquid is neutralized with dil. aq. ammonia, using congo-red as indicator; a drop or two of dil. nitric acid is then added until the colour is lilac. The whole is diluted to about 200 c.c. and slowly heated to 50°–60°. The precipitated bismuth ammonium molybdate is washed with a 3 per cent. soln. of ammonium nitrate, and dried in an air-bath at 160°. When ignited, there remains a pale yellow mass of $Bi_2O.4MoO_3$. The reaction was studied by E. H. Miller and H. Frank, and H. S. Riederer. F. Zambonini studied the thermal diagram, Fig. 27, of the system $Bi_2(MoO_4)_3$–$PbMoO_4$. The curve descends rapidly from the m.p., 1065°, of lead molybdate to a eutectic at 615° corresponding with about 71·5 mol. per cent. of the bismuth salt. It then rises rapidly to 643°, the m.p. of bismuth molybdate. No solid soln. are formed, or else the mutual solubility in the solid state is very small.

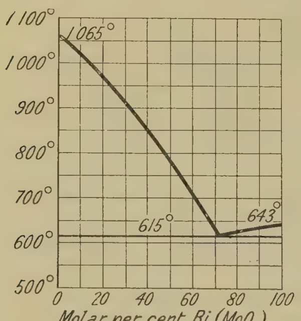


FIG. 27.—Freezing-point Curve of the System: $PbMoO_4$–$Bi_2(MoO_4)_3$.

The **vanadium molybdates** have been discussed in connection with vanadium—**9**. 54, 14; **columbium molybdate,** and **tantalum molybdate** have not been prepared; nor has the normal **chromium molybdate** been described, although A. Moberg,[19] and J. J. Berzelius, said that an apple-green precipitate is formed when ammonium molybdate is added to a soln. of chromic salt. H. Schultze could not prepare chromic molybdates by melting a mixture of chromic chloride and sodium molybdate. S. Prakash and N. R. Dhar obtained the hydrogel of chromic molybdate. The **chromatomolybdates** are discussed in connection with chromium; and some complex chromic dimolybdates are indicated below. The intermediate molybdenum oxides previously described can be regarded as molybdenum molybdates—*e.g.* Mo_5O_{14} can be represented as **molybdenyl molybdate;** $(MoO)_2(MoO_4)_3$; $Mo_{11}O_{32}$ as **molybdenum trimolybdate,** $(MoO)_2(Mo_3O_{10})_3$; Mo_9O_{26} as **molybdenyl paramolybdate,** $(MoO)_2(Mo_7O_{24})$; Mo_7O_{20} as **molybdenum molybdate,** $Mo_2(MoO_4)_5$; $Mo_{17}O_{50}$ as **molybdenum trimolybdate,** $Mo_2(Mo_3O_{10})_5$; and $Mo_{37}O_{120}$ as **molybdenum heptamolybdate,** $Mo_2(Mo_7O_{24})_5$. For the *tungsten molybdates,* see the molybdenum tungstates. A. Lancien[20] prepared **uranium molybdate,** $U(MoO_4)_2$, by reducing the paramolybdate with methyl, ethyl, or higher alcohols; and C. F. Rammelsberg obtained the *trihydrate,* as a greenish-black precipitate, by adding ammonium molybdate to an excess of uranium tetrachloride, and washing the precipitate with hot water. It loses 9·07 per cent. of water when calcined; and when melted, some molybdenum trioxide sublimes. Boiling alkali-lye extracts the molybdic acid; hydrochloric acid forms a green soln. which when diluted becomes yellow. A. Lancien prepared **uranyl molybdate,** $(UO_2)MoO_4$, as a precipitate by the addition of a soln. of ammonium molybdate to uranyl nitrate soln. When prepared in the dark, this compound forms a white, amorphous powder, which is reduced by ethyl and methyl alcohols or acetic acid to the green **uranous molybdate,** $U(MoO_4)_2$, this is then changed to a brick-red and then converted into the green oxide by prolonged boiling with alkali-lye and is rapidly dissolved with a yellowish-green fluorescence by hydrochloric, sulphuric, and nitric acids. When exposed to sunlight for thirty hours, uranyl molybdate becomes golden-yellow in colour, insoluble in nitric acid, which merely whitens it, and is no longer reduced by alcohol. Uranyl molybdate is radioactive, having an activity greater than that of the nitrate and equal to that of radium bromide of activity 40. B. Szilard prepared uranyl molybdate using an excess of uranyl nitrate, in one case, and, in the other case, an excess of ammonium molybdate, and found the radioactivity of both to be the same, and to be quite normal. The uranium molybdate obtained by P. P. Pilipenko from Bivongi was shown by G. Carobbi to be ferrimolybdate—*vide infra.*

J. B. Richter[21] treated a soln. of manganous chloride with potassium molybdate and obtained a brownish-white precipitate which dissolved in forty to fifty times its weight of water. H. Schultze prepared **manganous molybdate,** $MnMoO_4$, by melting together a mixture of sodium molybdate, sodium chloride, and manganous chloride (1 : 2 : 3), and washing the cold mass with water. Yellow, fusible monoclinic plates remain. The cold mass which has been fused contains reddish-brown plates and needles, and yellow crystals. The yellow crystals are soluble in cold, dil. hydrochloric acid, whilst the brown ones are not attacked. W. Jander discussed the lattice-structure, and the diffusion of the molybdate and tungstate, as well as the reaction $MgO+MnMoO_4=MnO+MgMoO_4$. H. Struve prepared the *hydrate,* $MnMoO_4.H_2O$, by treating manganous carbonate with potassium or sodium trimolybdate; and A. Coloriano, by treating manganous nitrate with ammonium paramolybdate, and boiling the amorphous powder in the mother-liquor so that it may crystallize. The white powder consists of microscopic prismatic plates; it loses no water at 100°; but at a higher temp., it loses water and becomes brown. It is sparingly soluble in boiling water. E. Marckwald obtained tabular crystals of the *tritapentahydrate* by allowing the decahydrate to stand exposed to air for some time; and the *decahydrate* as a white, amorphous precipitate by adding an eq. amount of sodium molybdate to a soln. of manganous sulphate.

E. Marckwald reported a number of complex salts. Orange-yellow crystals of **ammonium manganous molybdate,** $(NH_4)_2O.MnO.3MoO_3.2\frac{1}{2}H_2O$, was obtained from a cold, dil. soln. of manganese sulphate (15 grms.) and the eq. proportion of ammonium paramolybdate in 100 c.c. of water; $(NH_4)_2O.3MnO.6MnO_3.16H_2O$, in yellowish-white, prismatic crystals, from a soln. of manganese sulphate and ammonium paramolybdate in a sealed tube at 150° for 5 hrs.; $(NH_4)_2O.2MnO.6MoO_3.16H_2O$, in brownish-red needles, from cold soln. of 25 grms. of manganese sulphate and an eq. amount of ammonium paramolybdate in 50 c.c. of water; $(NH_4)_2O.2MnO.12MoO_3.22H_2O$, in hexagonal, yellow plates, from the mother-liquor of the preceding salt; and **sodium manganous molybdate,** $2Na_2O.MnO.6MoO_3.19H_2O$, in yellowish-white needles by the action of cold soln. of sodium dimolybdate and manganese sulphate. Our knowledge of the complex manganous molybdates is thus in an unsatisfactory state.

By boiling ammonium manganic molybdate with manganic hydroxide, treating the product with water, and evaporating the brown soln., H. Struve obtained brown, amorphous, **manganic molybdate,** $2Mn_2O_3.MoO_3.4H_2O$. H. Struve attempted to prepare *molybdic alums*, of the general formula $2R_2'O.R_2'''O_3.12MoO_3.nH_2O$, where R' represents K or NH_4, and R''', Fe, Al, or Cr. He obtained instead, compounds of the general type $5R'_2O.Mn_2O_3.16MoO_3.12H_2O$. Thus, by boiling a soln. of ammonium molybdate with manganic hydroxide, he obtained **ammonium manganic molybdate,** $5(NH_4)_2O.Mn_2O_3.16MoO_3.12H_2O$; and E. Péchard treated a hot soln. of ammonium molybdate and a manganous salt with a dil. soln. of potassium permanganate, and obtained red crystals of the salt $3(NH_4)_2O.MnO_2.12MoO_2.5H_2O$. C. Friedheim and M. Samelson did not agree with the analyses of either E. Péchard, or of H. Struve, and A. Rosenheim and H. Itzig represented E. Péchard's compound by the formula $2(NH_4)_2O.K_2O.Mn_2O_3.10MoO_3.5H_2O$, and by the action of potassium chloride this was converted into $3K_2O.MnO_2.8MoO_3.5H_2O$. A. Rosenheim added 2 mols of a soln. of manganous chloride to a cold, sat. soln. of ammonium paramolybdate, and obtained the complex salt $(NH_3)_3H_7[Mn''(MoO_4)_6].3H_2O$, which lost 3 mols. of water when kept for 3 days at 60°. The compound $4(NH_4)_2O.Mn_2O_3.13MoO_3.9H_2O$ was prepared by F. Zambonini and V. Cagliotti. It is said to be the compound prepared by H. Struve, C. Friedheim and M. Samelson, and C. Friedheim and O. Allemann. The manganese is said to be really present in the bi- and quadrivalent states so that, in harmony with H. Struve's opinion, the Mn_2O_3 in the formula represents MnO and MnO_2. The formula can therefore be written $(NH_4)_8[Mn^{\cdot\cdot\cdot\cdot}(Mo_2O_7)_6].Mn^{\cdot\cdot}MoO_4.9H_2O$, in harmony with E. Péchard's suggestion that the ratio $MnO_2 : MoO_3$ is 1 : 12 and that the compound is analogous to the silicomolybdates. H. Struve also obtained red crystals of **potassium manganic molybdate,** $2K_2O.MnO.MnO_2.9MoO_3.8H_2O$, by boiling a soln. of potassium trimolybdate with manganic hydroxide, or by the action of chlorine on a soln. of potassium trimolybdate and manganous sulphate. C. Friedheim and M. Samelson represented the composition of this salt by the formula $2K_2O.Mn_2O_3.16MoO_3.12H_2O$.

E. Péchard reported **permanganous molybdate,** $MnO_2.12MoO_3.10H_2O$, to be formed by treating the barium salt, suspended in water, with the theoretical quantity of sulphuric acid, and evaporating the clear liquor in vacuo. A. Rosenheim and H. Itzig denied the existence of this compound. C. Friedheim and M. Samelson, and C. Friedheim and O. Allemann prepared what they regarded as **permanganitomolybdates;** these are indicated below. As emphasized by A. Rosenheim, the test employed to determine the active oxygen of the manganese dioxide—distillation with potassium bromide and hydrochloric acid—is by no means satisfactory; and the question whether these compounds contain quadrivalent or tervalent manganese has not been satisfactorily answered. A. Rosenheim thinks that these salts may be more or less impure forms of $R_nH_{10-n}[Mn'''(MoO_4)_6]$; although complexes with quadrivalent cerium, thorium, and zirconium are known.

A mixture of a soln. of ammonium paramolybdate and manganous chloride with 18·5 per cent. of hydrogen dioxide yields **ammonium permanganitomolybdate,** $2(NH_4)_2O.MnO_2.7MoO_3.5H_2O$; a mixed soln. of potassium paramolybdate, manganous chloride and 2·5 per cent. of hydrogen dioxide yields **potassium permanganitomolybdate,**

$3K_2O.MnO_2.8MoO_3.3$ or $5H_2O$. E. Péchard also prepared this salt; a mixed soln. of ammonium permolybdate, and manganous and potassium chlorides yields **potassium ammonium permanganitomolybdate,** $3\{K_2,(NH_4)_2\}O.MnO_2.8MoO_3.4H_2O$; sodium manganous permanganitomolybdate and potassium chloride yield **sodium potassium manganous permanganitomolybdate,** $3(K_2,Na_2,Mn)O.MnO_2.8MoO_3.4H_2O$; a soln. of ammonium paramolybdate, manganous chloride, and 2·5 per cent. hydrogen dioxide yields **ammonium permanganitomolybdate,** $3(NH_4)_2O.MnO_2.9MoO_3.6$, 7, or $8H_2O$; when this salt or the ammonium manganous salt is treated with potassium chloride, it forms **potassium permanganitomolybdate,** $3K_2O.MnO_2.9MoO_3.5$ or $6H_2O$. R. D. Hall also prepared this salt; a soln. of sodium paramolybdate, manganous chloride and 3·5 per cent. hydrogen dioxide furnishes **sodium manganous permanganitomolybdate,** $3(Na_2,Mn)O.MnO_2.9MoO_3.15H_2O$; a soln. of ammonium paramolybdate, manganous chloride, and potassium persulphate yields **ammonium manganous permanganitomolybdate,** $3\{(NH_4)_2,Mn\}O.MnO_2.9MoO_3.6$ or $7H_2O$; if more potassium persulphate is used, **ammonium potassium manganous permanganitomolybdate,** $3\{(NH_4)_2,K_2,Mn\}O.MnO_2.9MoO_3.7H_2O$; and similarly, **potassium manganous permanganitomolybdate,** $3(K_2,Mn)O.MnO_2.9MoO_3.6$ or $7H_2O$, is formed. R. D. Hall also prepared this salt; and by treating it with barium chloride obtained **barium permanganitomolybdate,** $3BaO.MnO_2.9MoO_3.12H_2O$; a soln. of ammonium manganous molybdate and potassium permanganate, or a soln. of ammonium paramolybdate with potassium permanganate and alcohol yields **ammonium manganous permanganitomolybdate,** $3\{(NH_4)_2,Mn\}O.MnO_2.10MoO_3.8$ or $10H_2O$; a soln. of ammonium paramolybdate, manganous sulphate, and potassium permanganate yields **ammonium potassium manganous permanganitomolybdate,** $3\{(NH_4)_2,K,Mn\}O.MnO_2.10MoO_3.6$ or $10H_2O$; a soln. of ammonium permolybdate, and manganous chloride yields **ammonium manganous permanganitomolybdate,** $4\{(NH_4)_2,Mn\}O.MnO_2.10MoO_3.6H_2O$; a boiling soln. of ammonium paramolybdate, potassium permanganate, and alcohol yields **ammonium potassium permanganitomolybdate,** $4\{(NH_4)_2,K_2,Mn\}O.MnO_2.10MoO_3.5H_2O$; leaving a soln. of ammonium paramolybdate, and molybdic acid in contact with hydrated manganese dioxide for 4 months furnishes **ammonium manganous permanganitomolybdate,** $4\{(NH_4)_2,Mn\}O.MnO_2.11MoO_3.7H_2O$; by using more hydrogen dioxide than was employed in preparing the 3 : 1 : 9 : 6—salt **ammonium manganous permanganitomolybdate,** $4\{(NH_4)_2,Mn\}O.MnO_2.11MoO_3.8H_2O$, is obtained; and an analogous process yields **potassium manganous permanganitomolybdate,** $4(K_2,Mn)O.MnO_2.11MoO_3.11H_2O$. E. Péchard's $3K_2O.MnO_2.12MoO_3.4H_2O$ could not be prepared by A. Rosenheim and H. Itzig, or by C. Friedheim and M. Samelson. Nor could A. Rosenheim and H. Itzig prepare E. Péchard's $3Na_2O.MnO_2.12MoO_3.13H_2O$.

H. Struve,[22] and E. Steinacker found that a soln. of a molybdate or molybdic acid is reduced when treated with a ferrous salt; but H. Schultze obtained normal **ferrous molybdate,** $FeMoO_4$, by fusing a mixture of sodium chloride, ferrous chloride, and sodium molybdate. G. Tammann said that the reaction between ferrous oxide and molybdenum trioxide begins at about 320°; and that the heat of formation of $FeMoO_4$ is 13·5 Cals. C. W. Scheele obtained a brown precipitate by treating a soln. of ferric chloride with potassium molybdate; and E. Marckwald obtained normal **ferric molybdate,** $Fe_2(MoO_4)_3.42H_2O$, in this manner by treating 3 mols of sodium molybdate with 2 mols of ferric chloride. G. Tammann said that no reaction between ferric oxide and molybdenum trioxide occurs below 600°; and he added that the heat of formation of $Fe_2(MoO_4)_3.nH_2O$ is —29·3 Cals. S. Prakash and N. R. Dhar found that a soln. of 8 c.c. of M-$FeCl_3$, 4 c.c. of water, and 8 c.c. of a 10 per cent. soln. of potassium molybdate sets to a jelly in 10 hrs. The viscosities at 30° were:

Age .	0	15	32	68	128	158	188	300 min.
Viscosity	0·009966	0·01009	0·01029	0·01094	0·01442	0·01916	0·03526	0·10620

Some forms of molybdic ochre—*vide supra*, molybdenum trioxide—are mixtures of ferric molybdate and molybdic acid. P. P. Pilipenko obtained a mineral from the Alexyewsky Copper Mines of Jenissejsker, Siberia, which corresponds with $2Fe_2O_3.7MoO_3.19H_2O$, and W. T. Schaller, one from Hortense, Colorado, which corresponded with $Fe_2(MoO_4)_3.7\frac{1}{2}H_2O$, and other samples from Renfrew, Ontario, etc., approximating $Fe_2(MoO_4)_3.n(3H_2O)$, and previously regarded as molybdic ochre, or molybdite (*q.v.*). E. S. Simpson gave $(Fe_2O_3.4MoO_3.5H_2O)5H_2O$. P. P. Pilipenko named these minerals **ferrimolybdite.** G. Carobbi obtained a ferrimolybdate, $4Fe_2O_3.13MoO_3.44H_2O$, from Bivongi.

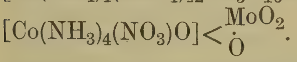
F. de Carli[23] observed that the reaction between cobaltous oxide and molybdenum trioxide begins at 410°. J. J. Berzelius obtained **cobaltous molybdate,** $CoMoO_4.nH_2O$, as a dirty yellow precipitate by adding a soln. of alkali molybdate to one of a cobaltous salt. The precipitate forms a red powder when dried, and it is decomposed by acids and alkali-lye. E. F. Smith and R. H. Bradbury found that cobalt molybdate is not formed either in cold dil. or conc. soln. By heating a conc. soln. of sodium molybdate with cobalt nitrate, a small quantity of a bluish-white precipitate is formed which dissolves again on cooling. H. Schultze obtained crystals of the anhydrous salt by melting together a mixture of normal sodium molybdate, cobaltous chloride, and sodium chloride (1 : 2 : 2). An impure cobaltous molybdate occurs as the mineral, named by W. Haidinger, **pateraite**—after A. Patera—in the Elias Mine, Joachimsthal. It was described by C. von Hauer, and J. von Jokély. An impure sample was analyzed by G. C. Laube.

A. Coloriano obtained the *monohydrate*, $CoMoO_4.H_2O$, or $HO.MoO_2.O.Co.OH$, in an amorphous state by the action of ammonium paramolybdate on a soln. of a cobaltous salt. When digested with water for a long time, it becomes crystalline. E. Marckwald said that the product is impure, and he prepared it by mixing a 6·5 per cent. soln. of cobaltous chloride with a 3·5 per cent. soln. of sodium molybdate in the cold, and in eq. proportions; the pale rose-coloured liquid was evaporated, at ordinary temp., over sulphuric acid, when the crystalline salt is formed. If the mixed soln. be heated on a water-bath with stirring a precipitate of the salt is obtained. E. Marckwald observed that the proportion of water in the salt may vary with the mode of preparation. The violet crystals lose part of their water at 150°, and all is expelled at 445°. The salt is almost insoluble in boiling water; it is decomposed by conc. acids with the separation of molybdenum trioxide, which, with more acid, may pass into soln. The salt is soluble in dil. acids. F. L. Sonnenschein digested freshly-precipitated cobaltous hydroxide with a small excess of aq. ammonia, and on evaporating the liquid obtained red, prismatic crystals of **cobaltous diamminomolybdate,** $CoMoO_4.2NH_3.H_2O$. If a large excess of aq. ammonia is employed a precipitate is produced. E. Marckwald also said that aq. ammonia dissolves cobaltous molybdate and the soln. on standing for some time deposits the diammine. S. H. C. Briggs prepared **ammonium cobaltous diamminomolybdate,** $(NH_4)_2Co(MoO_4)_2.2NH_3$, from a soln. of 20 grms. cobaltous sulphate, 50 grms. ammonium molybdate, 50 c.c. conc. aq. ammonia, and 90 c.c. of water. The liquid readily oxidizes, and it is evaporated over sulphuric acid, under reduced press. The salt is deposited in violet crystals which can be washed with dil. aq. ammonia, and dried with alcohol and ether.

N. S. Kurnakoff prepared **cobaltic molybdates,** by the action of bromine on a soln. of potassium or sodium molybdate. These salts differ from the cobaltous molybdates in giving off chlorine when they are boiled with hydrochloric acid. C. Friedheim and F. Keller found that **ammonium cobaltic dodecamolybdate,** $3(NH_4)_2O.Co_2O_3.12MoO_3.20H_2O$, or $(NH_4)_3H_6[Co(MoO_4)_6].7H_2O$, is obtained by adding a 30 per cent. of ammonium persulphate to a mixture of cobaltous acetate and ammonium paramolybdate, acidifying with dil. acetic acid, and then slowly heating. It may also be prepared by the action of cobaltous acetate on the ammonium permolybdate. It forms green, rhombic plates and dissolves in water to give a green soln. With conc. sulphuric acid, oxygen is evolved; ammonia is evolved by the action of potassium or sodium hydroxide. It is reduced by sulphurous acid. Hydrogen peroxide causes the evolution of oxygen whilst permolybdates are formed. By adding potassium chloride to an aq. soln. of ammonium cobaltic decamolybdate, olive-green crystals of **potassium cobaltic dodecamolybdate,** $3K_2O.Co_2O_3.12MoO_3.15H_2O$, or $K_3H_6[Co(MoO_4)_6].7H_2O$, are produced. By mixing cobaltous acetate, ammonium paramolybdate, and hydrogen dioxide dark green crystals of **ammonium cobalt decamolybdate,** $2(NH_4)_2O.Co_2O_3.10MoO_3.12H_2O$, or $(NH_4)_2H_6[Co(OH(MoO_4)_5].7H_2O$, are formed; and **potassium cobaltic decamolybdate,** $3K_2O.Co_2O_3.10MoO_3.11H_2O$, is obtained either from cobaltous acetate, potassium persulphate, and potassium paramolybdate or from cobaltous acetate and ammonium permolybdate and potassium chloride, or by the addition of potassium chloride to a cold sat. aq. soln. of ammonium cobaltic dodecamolybdate. By treating an aq. soln. of ammonium cobaltic decamolybdate with barium chloride, bright green **barium cobaltic enneamolybdate,** $3BaO.Co_2O_3.9MoO_3.25H_2O$, or $Ba_3H_5[Co(OH)(MoO_4)_5].3H_2O$, is formed; and if ammonium cobaltic dodecamolybdate is similarly treated, bright green **ammonium barium cobaltic decamolybdate,** $\frac{1}{2}(NH_4)_2O.1\frac{1}{2}BaO.Co_2O_3.10MoO_3.18\frac{1}{2}H_2O$, is produced.

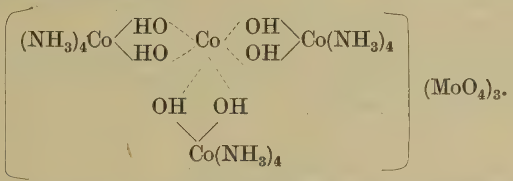
P. R. Ray and S. N. Maulik treated a mixture of a cobalt salt and normal sodium molybdate or molybdic acid in the presence of the calculated quantity of ammonium salt and ammonia, with a vigorous current of air, and crystallized the product from an ammoniacal soln. They thus obtained **cobaltic chloropentamminomolybdate,** $[CoCl(NH_3)_5]MoO_4$; **cobaltic hydroxypentamminomolybdate,** $[Co(OH)(NH_3)_5]MoO_4.H_2O$ (or $2{\cdot}5H_2O$); **cobaltic aquopentamminomolybdate,** $[Co(H_2O)(NH_3)_5]_2(MoO_4)_3$; **cobaltic thiocyanatopentamminomolybdate,** $[Co(SCy)(NH_3)_5]MoO_4$; and **cobaltic nitratopentamminomolybdate,** $[Co(NO_3)(NH_3)_5]MoO_4$; also **cobaltic molybdatopentamminomolybdate,** $[Co(MoO_4)(NH_3)_5]_2MoO_4$; **cobaltic aquonitritotetramminomolybdate,** $[Co(H_2O)(NO_2)(NH_3)_4]MoO_4$; and **cobaltic molybdatonitritotetramminomolybdate,** $[Co(MoO_4)(NO_2)(NH_3)_4]$.

B. K. Paul and P. V. Sarkar prepared **cobaltic dimolybdatotetramminotrimolybdate,** $[Co(NH_3)_4(Mo_2O_7)]Mo_3O_{10}.6H_2O$; **cobaltic molybdatotetramminomolybdate,** $[Co(NH_3)_4(MoO_4)]MoO_4.3H_2O$; **cobaltic molybdatotetramminotrimolybdate,** $[Co(NH_4)_4(MoO_4)]_2Mo_3O_{10}.4H_2O$; and **cobaltic nitratotetramminomolybdate,**



$[Co(NH_3)_4(NO_3)O]<^{MoO_2}_{O}$.

There are also complex salts of **cobaltic diaquotetramminomolybdatodimolybdate,** $[Co(NH_3)_4(H_2O)_2]_4(MoO_3)_3(Mo_2O_7)_3.3H_2O$; and of $[Co(NH_3)_4(H_2O)_2]_{12}(MoO_4)_{15}(Mo_2O_7)_3$. They also prepared **cobaltic hexahydroxydodecamminomolybdate,**



S. H. C. Briggs prepared **ammonium cobaltic aquopentamminomolybdate,** $[Co(NH_3)_5(H_2O)]_2(MoO_4)_3.(NH_4)_2MoO_4.2H_2O$, by allowing a soln. of ammonium cobaltous molybdate to oxidize in air when crimson needles are deposited. The salt dissolves in dil. aq. ammonia, but is slightly decomposed by water; and when boiled the soln. in potash-lye gives off ammonia and deposits cobaltic hydroxide.

F. de Carli [24] observed that the reaction between molybdenum trioxide and nickelous oxide begins about 495°. J. B. Richter, and C. Hatchett obtained a light green or white precipitate by adding potassium molybdate to a soln. of nickelous chloride. The precipitate was said to be slightly soluble in boiling water. E. Marckwald obtained **nickelous molybdate,** $NiMoO_4.\frac{2}{3}H_2O$, as a yellow mass by heating a soln. of nickelous chloride and normal sodium molybdate; with sodium dimolybdate, the precipitate was said to have $\frac{3}{4}H_2O$. This means that the precipitate from boiling soln. is probably anhydrous; if precipitated from cold soln., the salt was said to be a *pentahydrate.* The green pentahydrate forms a pale blue soln. with aq. ammonia. H. Schultze prepared monoclinic prisms of the anhydrous salt by fusing a mixture of sodium molybdate, nickelous chloride and sodium chloride, W. Jander discussed the lattice-structure; and the diffusion of the molybdate and tungstate. F. L. Sonnenschein obtained **nickelous diamminomolybdate,** $NiMoO_4.2NH_3.H_2O$, from a soln. of freshly-precipitated nickelous hydroxide or molybdate in aq. ammonia. It is decomposed by water. G. L. Clark found that **nickelous hexamminomolybdate,** $Ni(NH_3)_6MoO_4$, has a vap. press. of 760 mm. at

389°. S. H. C. Briggs prepared **ammonium nickelous diamminomolybdate,** $(NH_4)_2Ni(MoO_4)_2.2NH_3$, in green crystals, by allowing to stand in an open dish a soln. of 20 grms. of hexahydrated nickelous chloride in 15 c.c. of water, mixed with 50 grms. of ammonium molybdate in 70 c.c. of conc. aq. ammonia and 50 c.c. of water.

The **platinum molybdates** have not been prepared, but O. W. Gibbs [25] reported that complex platinic molybdates can be prepared by the action of platinic acid, platinates, or chloroplatinic acid on acid molybdates. The evidence for the individuality of these products, $R_2O : PtO_2 : MoO_3 : H_2O$, is inadequate. Two ammonium platinic molybdates were reported. The one 3 : 2 : 8 : 12 was obtained by boiling freshly-precipitated sodium platinate with a soln. of ammonium molybdate. The lemon-yellow crystals decompose when heated. The salt is sparingly soluble in water. It forms pale yellow *mercurous and mercuric salts* when treated respectively with mercurous and mercuric nitrates; pale yellow *silver salt,* by the action of silver nitrate; pale yellow *thallous salt,* by thallous nitrate; and it gives a pale yellow precipitate with cobaltic dinitritotetramminonitrate. The mother-liquid employed in the preparation of the 3 : 3 : 8 : 12-salt furnishes the 1 : 1 : 2 : $9\frac{1}{2}$-salt on evaporation. The brown oily liquid gradually dries to a dark brown mass which is decomposed by water. If hydrochloroplatinic acid be added to a boiling soln. of potassium molybdate in an excess of potash-lye, and the soln. acidified with acetic acid, it deposits a yellow, crystalline mass of **potassium platinic molybdate**—10 : 1 : 60 : 40—which is possibly a mixture of potassium hexamolybdate and the 2 : 1 : 12 : 4-salt. It decomposes when heated; it is easily soluble in hot water; a pale bluish-green *copper salt* is precipitated by cupric sulphate, and it is soluble in excess; silver nitrate gives a pale yellow crystalline *silver salt.* A soln. of platinic hydroxide forms an olive-green soln. with sodium molybdate. The soln. furnishes **sodium platinic molybdate**—4 : 1 : 10 : 29. The amber-yellow plates are very soluble in water, and it forms cryptocrystalline precipitates with metallic salt soln. When the *barium salt* is treated with dil. sulphuric acid, or the silver salt with dil. sulphuric acid, a soln. of the corresponding acid is obtained—*e.g.* $PtO_2.10MoO_3.4H_2O$, which can be regarded as a platinic molybdate. A. Rosenheim could not confirm these observations.

References.

[1] L. F. Svanberg and H. Struve, *Svenska Akad. Handl.*, **1**. 9, 1848; *Journ. prakt. Chem.*, (1), **44**. 257, 1848; *Phil. Mag.*, (3), **33**. 409, 524, 1848; J. C. G. de Marignac, *Compt. Rend.*, **42**. 288, 1856; *Arch. Sciences Genève*, (2), **14**. 271, 1855; M. Delafontaine, *ib.*, (2), **30**, 255, 1867; G. Wempe, *Zeit. anorg. Chem.*, **78**. 298, 1912; *Beiträge zur Kenntnis der Molybdate*, München, 1911; A. Werncke, *Zeit. anal. Chem.*, **14**. 12, 1875; H. P. Cady and R. Taft, *Journ. Phys. Chem.*, **29**. 1057, 1925; A. Rosenheim, *Zeit. anorg. Chem.*, **96**. 139, 1916; F. A. Flückiger, *Pogg. Ann.*, **86**. 594, 1852; W. Keferstein, *ib.*, **99**. 275, 1856; A. Winkler, *ib.*, **111**. 443, 1860; C. F. Rammelsberg, *ib.*, **128**. 311, 1866; H. Schröder, *Ber.*, **11**. 2211, 1878; J. W. Retgers, *Zeit. phys. Chem.*, **10**. 529, 1892; G. N. Wyrouboff, *Bull. Soc. Min.*, **13**. 77, 1893; R. E. Liesegang, *Phot. Arch.*, **34**. 179, 193, 1893; I. F. J. Kupfferschläger, *Bull. Soc. Chim.*, (2), **41**. 172, 1884; H. Stamm, *Ueber die Löslichkeit von Ammonsalzen und Alkalisalzen in wässerigen Ammoniak*, Halle, 1926; T. L. Phipson, *Chem. News*, **30**. 33, 1874; J. W. Thomas, *ib.*, **37**. 246, 1878; *Journ. Chem. Soc.*, **33**. 367, 1878; F. J. Faktor, *Pharm. Post*, **34**. 485, 1901; O. F. von der Pfordten, *Liebig's Ann.*, **237**. 201, 1886; O. Brunck, *ib.*, **336**. 281, 1904; P. Kulisch, *ib.*, **231**. 327, 1885; *Ueber die Einwirkung des Phosphorwasserstoffs auf Metallsalzlosungen*, Berlin, 1885; S. M. Jörgensen, *Journ. prakt. Chem.*, (2), **20**. 105, 1879; C. E. Guignet, *Compt. Rend.*, **108**. 178, 1889; M. Brand, *Ueber Molybdate, Sulfomolybdate und Phosphomolybdate des Lithiums*, Bern, 1905; F. Ephraim and M. Brand, *Zeit. anorg. Chem.*, **64**. 258, 1909; W. V. Bhagwat and N. R. Dhar, *Journ. Indian Chem. Soc.*, **6**. 781, 1929; A. S. Garnak, *Journ. Russ. Chem. Ind.*, **6**. 534, 1929; F. Krauss and E. Bruchhaus, *Zeit. anorg. Chem.*, **189**. 53, 1930; E. Bruchhaus, *Ueber Reaktionen zwischen gelösten Stoffen und Gasen bei Belichtung mit ultravioletten Strahlen*, Düsseldorf, 1930; P. Krishnamurti, *Indian Journ. Phys.*, **5**. 633, 1930.

[2] V. Kohlschütter and K. A. Hofmann, *Liebig's Ann.*, **307**. 314, 1899; G. Canneri, *Gazz. Chim. Ital.*, **57**. 872, 1927.

[3] L. F. Svanberg and H. Struve, *Svenska Akad. Handl.*, **1**. 9, 1848; *Journ. prakt. Chem.*, (1), **44**. 257, 1848; *Phil. Mag.*, (3), **33**. 409, 524, 1848; J. G. Gentele, *Journ. prakt. Chem.*, (1), **81**. 411, 1860; F. E. Zenker, *ib.*, (1), **58**. 490, 1853; P. Walden, *Zeit. phys. Chem.*, **1**. 74, 1887;

J. W. Retgers, *ib.*, **8**. 6, 1891 ; W. Herz, *ib.*, **98**. 98, 1921 ; H. E. Boeke, *ib.*, **56**. 686, 1906 ; *Zeit. anorg. Chem.*, **50**. 355, 1906 ; F. Ephraim and M. Brand, *ib.*, **64**. 258, 1900 ; E. Groschuff, *ib.*, **58**. 113, 1908 ; H. Grossmann, *ib.*, **41**. 47, 1904 ; F. M. Jäger, *ib.*, **101**. 1, 1917 ; F. M. Jäger and B. Kapma, *ib.*, **113**. 27, 1920 ; H. S. van Klooster, *ib.*, **85**. 49, 1914 ; G. Beck, *ib.*, **174**. 41, 1928 ; K. Seubert and W. Pollard, *ib.*, **8**. 296, 1895 ; L. Pissarjewsky, *ib.*, **24**. 108, 1900 ; K. Hüttner and G. Tammann, *ib.*, **43**. 215, 1905 ; G. Tammann, *Mem. Acad. St. Petersburg*, (7), **35**. 1, 1887 ; F. Ullik, *Sitzber. Akad. Wien*, **55**. 767, 1867 ; **60**. 295, 1869 ; *Liebig's Ann.*, **144**. 204, 320, 1867 ; **153**. 373, 1870 ; L. I. Dana and P. D. Foote, *Trans. Faraday Soc.*, **15**. 186, 1920 ; J. Ohly, *Chem. Ztg.*, **22**. 40, 1898 ; I. Traube, *Zeit. anorg. Chem.*, **8**. 12, 1895 ; *Ber.*, **24**. 374, 1891 ; R. Funk, *ib.*, **33**. 3698, 1900 ; E. Blanc, *Journ. Chim. Phys.*, **18**. 28, 1920 ; W. Zachariassen, *Norsk. Geol. Tids.*, **9**. 65, 1926 ; M. Delafontaine, *Journ. prakt. Chem.*, (1), **95**. 136, 1865 ; *Liebig's Ann.*, **127**. 293, 1866 ; *Arch. Sciences Genève*, (2), **23**. 5, 1865 ; (2), **30**. 232, 1867 ; G. Wempe, *Beiträge zur Kenntnis der Molybdate*, München, 1911 ; *Zeit. anorg. Chem.*, **78**. 298, 1912 ; R. Lorenz and W. Herz, *ib.*, **120**. 322, 1922 ; **135**. 374, 1924 ; **138**. 330, 1924 ; L. Ott, *Elektrolyse geschmolzener Molybdate und Vanadate*, München, 1911 ; J. Terwelp, *Beiträge zur Elektrochemie der Molybdate*, Berlin, 1903 ; A. Piutti, *Radium*, **8**. 13, 1911 ; A. Junius, *Beiträge zur Kenntnis der Molybdate*, Berlin, 1905 ; *Zeit. anorg. Chem.*, **46**. 428, 1905 ; W. J. Baragiola, *Ueber das Verhalten der normalen Natrium- und Kaliumsalze des Wolframs, Molybdäns, und Vanadins gegen Ammoniumchlorid*, Bern, 1902 ; M. Amadori, *Atti Accad. Lincei*, (5), **21**. i, 667, 1912 ; (5), **22**. i, 453, 1609, 1913 ; (5), **23**. i, 707, 800, 1914 ; W. G. Mixter, *Amer. Journ. Science*, (4), **29**. 488, 1910 ; A. Hare, *Phil. Mag.*, (6), **48**. 412, 1924 ; J. J. Coleman, *ib.*, (5), **23**. 1, 1887 ; P. Blackman, *Journ. Phys. Chem.*, **13**. 151, 1909 ; E. Darmois and J. Périn, *Compt. Rend.*, **177**. 762, 1923 ; A. Rosenheim and W. Reglin, *Zeit. anorg. Chem.*, **120**. 103, 1921 ; F. Hoermann, *ib.*, **177**. 145, 1928 ; *Beitrag zur Kenntnis der Molybdate und Wolframate*, Leipzig, 1928 ; W. V. Bhagwat and N. R. Dhar, *Journ. Indian Chem. Soc.*, **6**. 781, 1929 ; J. C. G. de Marignac, *Compt. Rend.*, **42**. 288, 1856 ; *Arch. Sciences Genève*, (2), **14**. 271, 1855 ; G. Jander and A. Winkel, *Zeit. phys. Chem.*, **149**. 97, 1930 ; G. Jander, K. R. Jahr and W. Heukeshoven, *Zeit. anorg. Chem.*, **194**. 383, 1930 ; G. Jander and W. Heukeshoven, *ib.*, **187**. 60, 1930.

[4] A. Piccini, *Atti Accad. Lincei*, (5), **7**. i, 267, 1892 ; *Zeit. anorg. Chem.*, **1**. 51, 1892 ; F. Ephraim and H. Herschfinkel, *ib.*, **64**. 266, 1909 ; H. Herschfinkel, *Ueber Molybdate, Sulfomolybdate, Phosphormolybdate und Arsenmolybdate*, Bern, 1907 ; J. W. Retgers, *Zeit. phys. Chem.*, **8**. 6, 1891.

[5] G. Jörgensen, *Tids. Fis. Kemi*, **1**. 187, 1896 ; H. Debray, *Compt. Rend.*, **96**. 1616, 1883 ; S. H. C. Briggs, *Journ. Chem. Soc.*, **85**. 674, 1904 ; H. Struve, *Bull. Acad. St. Petersburg*, **12**. 142, 1854 ; G. Tammann, *Zeit. anorg. Chem.*, **149**. 21, 1925 ; J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817 ; *Pogg. Ann.*, **4**. 153, 1825 ; **6**. 369, 1826 ; **7**. 261, 1826 ; *Ann. Chim. Phys.*, (2), **17**. 5, 1821.

[6] J. B. Richter, *Ueber die neueren Gegenstände der Chemie*, Breslau, **1**. 49, 1791 ; **2**. 97, 1792 ; **10**. 86, 1802 ; C. W. Scheele, *Svenska Akad. Handl.*, (1), **39**. 247, 1778 ; (1), **40**. 238, 1779 ; H. Rose, *Pogg. Ann.*, **40**. 400, 1837 ; F. Wöhler and F. Rautenberg, *Liebig's Ann.*, **114**. 119, 1860 ; L. F. Svanberg and H. Struve, *Svenska Akad. Handl.*, (2), **1**. 9, 1848 ; *Journ. prakt. Chem.*, (1), **44**. 257, 1848 ; *Phil. Mag.*, (3), **33**. 409, 524, 1848 ; E. F. Smith and R. H. Bradbury, *Ber.*, **24**. 3074, 1891 ; J. Krutwig, *ib.*, **14**. 304, 1811 ; W. Muthmann, *ib.*, **20**. 983, 1887 ; *Zeit. Kryst.*, **15**. 387, 1889 ; H. Debray, *Compt. Rend.*, **66**. 732, 1868 ; O. Widman, *Bull. Soc. Chim.*, (2), **20**. 64, 1873 ; R. W. G. Wyckoff, *Journ. Amer. Chem. Soc.*, **44**. 1994, 1922 ; P. P. Ewald, *Zeit. Kryst.*, **61**. 1, 1924 ; P. Ray and J. Dasgupta, *Journ. Indian Chem. Soc.*, **5**. 519, 1928.

[7] J. B. Richter, *Ueber die neueren Gegenstände der Chemie*, Breslau, **1**. 49, 1791 ; **2**. 97, 1792 ; **10**. 86, 1802.

[8] E. Cane, *Rend. Accad. Napoli*, (3), **32**. 83, 1926 ; L. Vegard, *Phil. Mag.*, (7), **1**. 1151, 1926 ; L. Vegard and A. Refsum, *Norske Vid. Akad. Skr. Oslo*, 2, 1927 ; E. K. Broch, *ib.*, 8, 1929 ; A. Kissock, *Brit. Pat. No.* 276155, 1926 ; *Chem. Met. Engg.*, **22**. 1018, 1920 ; L. F. Svanberg and H. Struve, *Svenska Akad. Handl.*, **1**. 9, 1848 ; *Journ. prakt. Chem.*, (1), **44**. 257, 1848 ; *Phil. Mag.*, (3), **33**. 409, 524, 1848 ; F. Ullik, *Sitzber. Akad. Wien*, **55**. 767, 1867 ; **60**. 295, 1869 ; *Liebig's Ann.*, **144**. 204, 320, 1867 ; **153**. 373, 1870 ; E. F. Smith and R. H. Bradbury, *Ber.*, **24**. 3074, 1891 ; H. Schultze, *Ueber die Darstellung krystallisirter Verbindungen insbesondere über einige krystallisirte molybdänsaure und wolframsaure Salze*, Göttingen, 1862 ; *Liebig's Ann.*, **126**. 49, 1863 ; H. Traube, *Centr. Min.*, 679, 1901 ; T. H. Hiortdahl, *Zeit. Kryst.*, **12**. 411, 1887 ; E. Herlinger, *ib.*, **62**. 454, 1925 ; L. Michel, *Bull. Soc. Min.*, **17**. 612, 1894 ; *Recherches sur quelques tungstates, molybdates, séléniates, tellurates cristallisés*, Paris, 1889 ; L. Kahlenberg and W. J. Trautmann, *Trans. Amer. Electrochem. Soc.*, **39**. 377, 1921 ; F. de Carli, *Atti Accad. Lincei*, (6), **1**. 533, 1925 ; D. Balareff, *Zeit. anorg. Chem.*, **138**. 349, 1924 ; **145**. 117, 1925 ; J. A. Hedvall and N. von Zweigbergh, *ib.*, **108**. 119, 1919 ; G. Tammann, *ib.*, **149**. 21, 1925 ; W. Jander, *ib.*, **163**. 1, 1927 ; **166**. 50, 1927 ; **174**. 11, 1928 ; **190**. 397, 1930 ; **191**. 171, 1930 ; **192**. 286, 295, 1930 ; W. Jander and W. Stamm, *ib.*, **190**. 65, 1930 ; F. W. Clarke, *Amer. Journ. Science*, (3), **14**. 280, 1877 ; E. S. Larsen, *Bull. U.S. Geol. Sur.*, 679, 1921 ; F. Zambonini, *Rev. Min. Crist. Ital.*, **45**. 1, 1915 ; *Compt. Rend.*, **162**. 835, 1916 ; C. J. Heine, *Journ. prakt. Chem.*, (1), **9**. 204, 1836 ; J. W. Retgers, *Zeit. phys. Chem.*, **8**. 6, 1891 ; P. P. Pilipenko, *Bull. Tomsk. Univ.*, 63, 1915 ; W. H. Melville, *Amer. Journ. Science*, (3), **41**. 138, 1891 ; F. Zambonini and R. G. Levi, *Atti Accad. Lincei*, (6), **2**. 149, 225, 303, 1925 ; V. G. Aranda, *Anal. Fis. Quim.*, **28**. 165, 1929 ; T. Westphal, *Beitrage zur Kenntnis der molybdansäuren Salze*, Berlin, 46, 1895 ; H. Mabee, *Canada Dept. Mines Ores Investigations*, 156, 1928 ; D. Balareff and N. Lukova, *Koll. Zeit.*, **52**. 222, 1930.

[9] A. Atterberg, *Svenska Akad. Handl.*, **12**. 5, 1873 ; *Oefvers. Akad. Stockholm*, **30**. 4, 1873 ; A. Rosenheim and P. Woge, *Zeit. anorg. Chem.*, **15**. 283, 1897 ; G. Tammann, *ib.*, **149**. 21, 1925.

[10] M. Delafontaine, *Arch. Sciences Genève*, (2), **30**. 238, 1867 ; H. Struve, *Bull. Acad. St. Petersburg*, (2), **12**. 145, 1853 ; *Journ. prakt. Chem.*, (1), **61**. 453, 1854 ; F. Ullik, *Liebig's Ann.*, **144**. 212, 1867 ; **153**. 373, 1870 ; *Sitzber. Akad. Wien*, **55**. 767, 1867 ; **60**. 295, 1869 ; V. von Zepharovich, *ib.*, **58**. 115, 1868 ; F. de Carli, *Atti Accad. Lincei*, (6), **1**. 533, 1925 ; G. N. Wyrouboff, *Bull. Soc. Min.*, **12**. 60, 1889 ; *Bull. Acad. Min.*, (3), **2**. 500, 1889 ; A. and E. Scacchi, *Atti Accad. Napoli*, (2), **1**. 1, 1886 ; F. Westphal, *Beiträge zur Kenntnis der molybdänsauren Salze*, Berlin, 46, 1895 ; G. Wempe, *Beiträge zur Kenntnis der Molybdate*, München, 1911 ; *Zeit. anorg. Chem.*, **78**. 298, 1912 ; G. Tammann, *ib.*, **149**. 21, 1925 ; W. Jander, *ib.*, **190**. 397, 1930 ; **191**. 171, 1930 ; **192**. 286, 295, 1930 ; E. K. Broch, *Norske Vid. Akad. Skr.*, 8, 1929 ; F. Rodolico, *Atti Accad. Lincei*, (6), **7**. 660, 1928.

[11] R. Brandes, *Schweigger's Journ.*, **29**. 325, 331, 1820 ; H. Schultze, *Ueber die Darstellung krystallisirter Verbindungen insbesondere über einige krystallisirte molybdänsaure und wolframsaure Salze*, Göttingen, 1862 ; *Liebig's Ann.*, **126**. 49, 1863 ; A. Coloriano, *Bull. Soc. Chim.*, (2), **50**. 451, 1888 ; F. L. Sonnenschein, *Journ. prakt. Chem.*, (1), **53**. 339, 1851 ; E. Manassewitsch, *Beiträge zur Kenntnis der Molybdate des Zinks und Cadmiums*, Bern, 1900 ; A. Junius, *Beiträge zur Kenntnis des Molybdates*, Berlin, 1905 ; *Zeit. anorg. Chem.*, **46**. 428, 1905 ; E. F. Smith and R. H. Bradbury, *Ber.*, **24**. 3074, 1891 ; S. H. C. Briggs, *Journ. Chem. Soc.*, **85**. 674, 1904 ; F. de Carli, *Atti Accad. Lincei*, (6), **1**. 533, 1925 ; W. Jander, *Zeit. anorg. Chem.*, **190**. 397, 1930 ; **191**. 171, 1930 ; **192**. 286, 295, 1930 ; E. K. Broch, *Norske Vid. Akad. Skr.*, 8, 1929.

[12] H. Struve, *Bull. Acad. St. Petersburg*, (2), **12**. 142, 1854 ; *Journ. prakt. Chem.*, (1), **61**. 453, 1854 ; J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817 ; *Pogg. Ann.*, **4**. 153, 1825 ; **6**. 331, 369, 1826 ; **7**. 261, 1826 ; *Ann. Chim. Phys.*, (2), **17**. 5, 1821 ; C. Hatchett, *Phil. Trans.*, **95**. 323, 1795 ; C. W. Scheele, *Svenska Akad. Handl.*, **39**. 247, 1778 ; **40**. 238, 1779 ; C. H. Hirzel, *Ueber die Einwirkungen des Quecksilberoxyds auf des Ammoniak und die Ammoniaksalze*, Leipzig, 1852 ; *Liebig's Ann.*, **84**. 267, 1852.

[13] C. Renz, *Beiträge zur Kenntnis des Indiums und Thalliums*, Breslau, 1902 ; *Ber.*, **34**. 3765, 1901 ; **36**. 4394, 1903 ; H. Struve, *Bull. Acad. St. Petersburg*, (2), **12**. 142, 1854 ; *Journ. prakt. Chem.*, (1), **61**. 453, 1854 ; J. G. Gentele, *ib.*, (7), **81**. 411, 1860 ; G. Tammann, *Zeit. anorg. Chem.*, **149**. 21, 1925 ; M. Delafontaine, *Arch. Sciences Genève*, (2), **30**. 232, 1867 ; P. S. Oettinger, *Zeit. Chem.*, (1), **7**. 440, 1864 ; *On the Combinations of Thallium*, Berlin, 1864 ; H. Flemming, *Jena Zeit.*, **4**. 33, 1868 ; *Bull. Soc. Chim.*, (2), **10**. 235, 1868 ; F. Mauro, *Atti Accad. Lincei*, (5), **2**. ii, 382, 1892.

[14] P. Didier, *Compt. Rend.*, **102**. 823, 1886 ; A. Cossa, *ib.*, **98**. 990, 1884 ; **102**. 1315, 1886 ; *Atti Accad. Lincei*, (4), **2**. i, 320, 1886 ; *Gazz. Chim. Ital.*, **16**. 284, 1886 ; G. Carobbi, *ib.*, **58**. 53, 1928 ; H. Traube, *Centr. Min.*, 679, 1901 ; F. T. Frerichs and E. F. Smith, *Liebig's Ann.*, **191**. 331, 1878 ; E. Cane, *Rend. Accad. Napoli*, (3), **32**. 83, 1926 ; P. T. Cleve, *Bull. Soc. Chim.*, (4), **43**. 53, 1885 ; *Chem. News*, **53**. 93, 1886 ; A. Cleve, *Oefvers. Akad. Förh.*, **58**. 573, 1902 ; *Zeit. anorg. Chem.*, **32**. 129, 1902 ; G. Tammann, *ib.*, **149**. 21, 1925 ; G. Tammann and W. Rosenthal, *ib.*, **156**. 20, 1926 ; F. R. M. Hitchcock, *Journ. Amer. Chem. Soc.*, **17**. 520, 1895 ; F. Zambonini and R. G. Levi, *Atti Accad. Lincei*, (6), **2**. 149, 377, 462, 1925 ; F. Zambonini, *Sulle soluzioni solide dei composti di calcio, stronzio, bario, e piombo con quelli delle " terre rare " e loro importanza per la mineralogia chimica*, Padova, 1915 ; *Riv. Min. Crist. Ital.*, **45**. 1, 1915 ; *Zeit. Kryst.*, **58**. 226, 1923 ; E. Herlinger, *ib.*, **62**. 454, 1925 ; S. Prakash and N. R. Dhar, *Journ. Indian Chem. Soc.*, **7**. 367, 1930.

[15] O. Kulka, *Beiträge zur Kenntnis einiger Zirkonium verbindungen*, Bern, 1902 ; J. J. Berzelius, *Svenska Akad. Handl.*, 1, 1829 ; *Pogg. Ann.*, **16**. 385, 1829 ; F. Zambonini, *Atti Accad. Lincei*, (5), **32**. i, 518, 1923 ; *Gazz. Chim. Ital.*, **54**. 39, 1924 ; *Compt. Rend.*, **176**. 1473, 1923 ; J. J. Chydenius, *ib.*, **119**. 43, 1863 ; *Kemisk Undersökning af Thorjord och Thorsalter*, Helsinfors, 1861 ; *Journ. prakt. Chem.*, (1), **89**. 464, 1863 ; S. M. Tanatar and E. K. Kurowsky, *Journ. Russ. Phys. Chem. Soc.*, **41**. 813, 1909 ; S. Prakash and N. R. Dhar, *Journ. Indian Chem. Soc.*, **6**. 587, 1929 ; **7**. 367, 417, 1930.

[16] J. B. Richter, *Ueber die neueren Gegenstände der Chemie*, Breslau, **1**. 49, 1791 ; **2**. 97, 1792 ; **10**. 86, 1802 ; J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817 ; *Pogg. Ann.*, **4**. 153, 1825 ; **6**. 331, 369, 1826 ; **7**. 261, 1826 ; *Ann. Chim. Phys.*, (2), **17**. 5, 1821 ; F. de Carli, *Atti Accad. Lincei*, (6), **1**. 533, 1925 ; H. Schiff, *Liebig's Ann.*, **120**. 47, 1861 ; J. P. Longstaff, *Chem. News*, **80**. 282, 1899 ; G. Denigès, *Journ. Pharm. Chim.*, (5), **30**. 207, 1894 ; S. Prakash and N. R. Dhar, *Journ. Indian Chem. Soc.*, **6**. 307, 587, 1929 ; **7**. 367, 1930.

[17] G. Bischof, *Lehrbuch der chemischen und physikalischen Geologie*, Bonn, **3**. 1980, 1855 ; A. W. Stelzner-Bergeat, *Die Erzlagerstätten*, Leipzig, 543, 1904 ; A. Himmelbauer, *Tschermak's Mitt.*, (2), **26**. 491, 1907 ; A. Sigmund, *ib.*, (2), **23**. 87, 1904 ; C. Bärwald, *Beiträge zur Kenntnis Molybdäns*, Berlin, 1885 ; *Ber.*, **17**. 1206, 1884 ; J. F. L. Hausmann, *Nachr. Gött.*, 217, 1851 ; *Liebig's Ann.*, **81**. 219, 1852 ; F. Wöhler, *ib.*, **102**. 283, 1856 ; N. S. Manross, *ib.*, **81**. 243, 1852 ; **82**. 358, 1852 ; E. Flint, *Comm. Mineral Museum Univ. Moscow*, 51, 1919 ; *Collect. Min. Lab. Moscow*, 51, 1917 ; A. Schrauf, *Sitzber. Akad. Wien*, **63**. 184, 1871 ; *Proc. Roy. Soc.*, **19**. 451, 1871 ; L. Bach, *Neues Jahrb. Min. B.B.*, **54**. 380, 1926 ; R. G. Dickinson, *Journ. Amer. Chem. Soc.*, **42**. 85, 1920 ; J. J. Saslawsky, *Zeit. Kryst.*, **59**. 170, 1923 ; L. Fletcher, *Min. Mag.*, **8**. 171, 1889 ; H. C. Sorby, *ib.*, **2**. 1, 1878 ; L. J. Spencer, *ib.*, **20**. 67, 1923 ; H. Kopp, *Liebig's Ann. Suppl.*, **3**. 107, 396, 1865 ; C. Doelter, *Das Radium und die Farben ; Einwirkung des Radiums und ultravioletter Strahlen auf*

organische und anorganische Stoffe sowie auf Mineralien, Dresden, 1910; G. Rose, *Reise nach dem Ural, dem Altai, und dem kaspischen Meere*, Berlin, **2**. 10, 1842; *Pogg. Ann.*, **46**. 639, 1839; H. Dauber, *ib.*, **107**. 267, 1859; C. Hatchett, *Phil. Trans.*, **95**. 323, 1795; J. F. W. Johnston, *Phil. Mag.*, (3), **12**. 387, 1838; F. N. Guild and F. S. Wartmann, *Amer. Min.*, **6**. 167, 1921; J. Guillissen, *Bull. Acad. Belg.*, **13**. 233, 1927; I. Domeyko, *Elementos de mineralojia*, Santiago, 1879; *Ann. Mines*, (4), **3**. 15, 1843; I. Eques a Born, *Lythophylacium Bornianum*, Prague, **1**. 90, 1772; J. B. L. Romé de l'Isle, *Cristallographie*, Paris, **3**. 387, 1783; F. S. Beudant, *Traité élémentaire de minéralogie*, Paris, **2**. 664, 1832; W. Haidinger, *Handbuch der bestimmenden Mineralogie*, Wien, 504, 1841; R. Kirwan, *Elements of Mineralogy*, London, **2**. 212, 1796; A. G. Werner, *Berg. Journ.*, **2**. 384, 1789; N. J. von Jacquin, *Miscellanea austriaca*, Wien, **2**. 139, 1781; F. X. Wulfen, *Abhandlung vom kärnthner Bleyspate*, Wien, 1785; A. des Clozieaux, *Nouvelles recherches sur les propriétés optiques des cristaux*, Paris, **2**. 18, 1859; A. Damour and A. des Cloizeaux, *Ann. Chim. Phys.*, (3), **51**. 445, 1857; E. Jannetez, *Compt. Rend.*, **114**. 1352, 1892; J. C. H. Heyer, *Crell's Ann.*, i, 58, 1790; M. H. Klaproth, *ib.*, i, 297, 1790; F. Göbel, *Schweigger's Journ.*, **37**. 71, 1823; *Phil. Mag.*, **62**. 187, 1823; C. L. Allen, *Chem. News*, **44**. 203, 1881; B. K. Emerson, *Bull. U.S. Geol. Sur.*, 126, 1895; E. F. Smith, *Journ. Amer. Chem. Soc.*, **20**. 245, 1898; J. L. Smith, *Amer. Journ. Science*, (2), **20**. 245, 1855; C. A. Ingersoll, *ib.*, (3), **48**. 193, 1894; F. Jost, *Zeit. Kryst.*, **7**. 592, 1883; E. Hunek, *ib.*, **49**. 11, 1911; E. Dittler, *ib.*, **53**. 167, 1914; **54**. 339, 1915; T. H. Hiortdahl, *ib.*, **12**. 411, 1887; F. Reinitzer, *ib.*, **8**. 587, 1884; *Lotos*, **31**. 1, 1883; V. von Zepharovich, *ib.*, **31**. 1, 1883; *Sitzber. Akad. Wien*, **54**. 278, 1866; *Zeit. Kryst.*, **8**. 587, 1884; V. von Kokscharoff, *Proc. Russ. Min. Soc.*, **18**. 145, 1882; *Materialen zur Mineralogie Russlands*, St. Petersburg, **8**. 408, 1883; E. Tacconi, *Atti Accad. Lincei*, (5), **9**. i, 22, 1900; E. Pelloux, *ib.*, (5), **9**. ii, 13, 1900; A. Pochettino, *ib.*, (5), **13**. i, 301, 1904; P. Comucci, *ib.*, (6), **3**. i, 335, 1926; E. Artini, *Rend. Ist. Lombardo*, **33**. 1179, 1900; *Riv. Min. Ital.*, **16**. 25, 1896; F. Zambonini, *ib.*, **45**. 1, 1915; *Sulle soluzioni solide die composti di calcio, stronzio, bario, e piombo con quelli delle " terre rare " e loro importanza per la mineralogia chimica*, Padova, 1915; *Bull. Soc. Min.*, **38**. 213, 1915; *Riv. Min. Crist. Ital.*, **45**. 1, 1915; *Zeit. Kryst.*, **58**. 226, 1923; F. Zambonini and R. G. Levi, *Atti Accad. Lincei*, (6), **2**. 462, 1925; E. Repossi, *Atti Soc. Milano*, **43**. 432, 1905; G. Cesaro, *Bull. Acad. Belg.*, 327, 1905; *Bull. Soc. Min.*, **31**. 257, 1908; A. de Gramont, *ib.*, **16**. 127, 1893; H. Regnard, *ib.*, **5**. 3, 1882; J. Couyat, *ib.*, **35**. 563, 1912; A. Lacroix, *ib.*, **6**. 80, 1883; A. Johnsen, *Centr. Min.*, 712, 1908; M. Bamberger and R. Grengg, *ib.*, 65, 1921; C. Schmidt, *Eclogae Geol. Helvetiæ*, **7**. 139, 1901; **38**. 200, 1904; *Zeit. prakt. Geol.*, **23**. 93, 1915; M. Henglein, *ib.*, **21**. 6, 1913; H. Traube, *Neues Jahrb. Min. B.B.*, **10**. 457, 1896; *Centr. Min.*, 679, 1901; F. M. Jäger and H. Haga, *Proc. Acad. Amsterdam*, **18**. 1350, 1916; S. Koch, *Ueber den Wulfenit*, Marburg, 1882; *Zeit. Kryst.*, **6**. 393, 1882; P. Groth, *ib.*, **7**. 592, 1883; *Chemische Krystallographie*, Leipzig, **2**. 395, 1908; L. F. Svanberg and H. Struve, *Svenska Akad. Handl.*, **1**. 9, 1848; *Journ. prakt. Chem.*, (1), **44**. 257, 1848; *Phil. Mag.*, (3), **33**. 409, 524, 1848; J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1818; **23**. 186, 1818; *Lehrbuch der Chemie*, Dresden, **2**. 353, 1844; **3**. 1208, 1845; *Pogg. Ann.*, **8**. 23, 1826; A. Drian, *Minéralogie et petrologie des environs de Lyon*, Lyons, 1849; H. C. Germs, *De thermische Analyse van Loodsulfaat, -Chromaat, -Molybdaat en -Wolframaat en van hun Binaire Combinaties*, Groningen, 1917; F. M. Jäger and H. C. Germs, *Zeit. anorg. Chem.*, **119**. 157, 1921; A. Junius, *ib.*, **46**. 433, 1905; *Beiträge zur Kenntnis der Molybdate*, Berlin, 15, 1905; G. Wempe, *Beiträge zur Kenntnis der Molybdate*, München, 63, 1911; *Zeit. anorg. Chem.*, **78**. 298, 1912; C. F. Rammelsberg, *Handbuch der Mineralchemie*, Leipzig, **2**. 283, 1875; G. Tammann, *Zeit. anorg. Chem.*, **149**. 21, 1925; D. Balareff, *ib.*, **153**. 184, 1926; H. B. Weiser, *Journ. Phys. Chem.*, **20**. 640, 1916; N. R. Dhar and S. Ghosh, *Zeit. anorg. Chem.*, **152**. 405, 1926; W. Jander, *ib.*, **174**. 11, 1928; A. Coloriano, *Bull. Soc. Chim.*, (2), **50**. 452, 1888; A. Terreil, *ib.*, (2), **13**. 115, 1870; A. Cossa, *Atti Accad. Lincei*, (4), i, 320, 1886; *Gazz. Chim. Ital.*, **16**. 234, 1886; L. Francesconi, L. Granata, A. Nieddu and G. Angelino, *ib.*, **48**. i, 112, 1918; F. de Carli, *Atti Accad. Lincei*, (6), **1**. 533, 1925; W. Meyerhoffer, *Zeit. phys. Chem.*, **38**. 323, 1901; A. P. Honess, *The Nature, Origin and Interpretation of the Etch Figures on Crystals*, New York, 92, 1927; G. Carobbi, *Ann. Chim. Applicata*, **18**. 485, 1928; V. G. Aranda, *Anal. Fis. Quim.*, **27**. 165, 251, 1929; E. E. Fairbanks, *Econ. Geol.*, **21**. 399, 1926; H. C. Bolton, *Ann. New York Acad.*, **1**. 1, 1879; **2**. 1, 1882; *Chem. News*, **36**. 249, 260, 1877; **37**. 14, 24, 65, 86, 98, 148, 1878; **43**. 31, 39, 1881; **47**. 251, 1883; *Min. Mag.*, **1**. 136, 1877; **4**. 181, 1882; *Ber.*, **13**. 733, 1880; K. Schlier, *Oesterr. Zeit. Berg. Hütt.*, **59**. 475, 1911; A. Maier, *Zeit. Kryst.*, **58**. 106, 1923; P. Ites, *Ueber die Abhängigkeit der Absorption des Lichtes von der Farbe in kristallinischen Körpern*, Göttingen, 1903; *Zeit. Kryst.*, **41**. 303, 1906; L. Kahlenberg and W. J. Trautmann, *Trans. Amer. Electrochem. Soc.*, **39**. 377, 1921; H. Schultze, *Ueber die Darstellung krystallisirter Verbindungen, insbesondere über einige krystallisirte molybdänsaure und wolframsaure Salze*, Göttingen, 1862; *Liebig's Ann.*, **126**. 49, 1863; E. Cane, *Rend. Accad. Napoli*, (3), **32**. 83, 1926; R. Pohl, *Phys. Zeit.*, **21**. 628, 1920; T. M. Chatard, *Amer. Journ. Science*, (2), **1**. 416, 1876; *Ber.*, **4**. 230, 1871; E. F. Smith and R. H. Bradbury, *ib.*, **24**. 2930, 1891; D. Vorländer and H. Hempel, *ib.*, **60**. B, 845, 1927; M. Kuhara, *Mem. Coll. Kyoto*, **3**. 71, 1918; M. L. Huggins, *Phys. Rev.*, (2), **21**. 719, 1923; T. W. Case, *ib.*, (2), **9**. 305, 1917; W. Schneider, *Zeit. Physik*, **51**. 266, 1928; O. G. Padurova, *Mem. Soc. Russ. Min.*, (2), **58**. 109, 1929; H. H. Willard and J. L. Kassner, *Journ. Amer. Chem. Soc.*, **52**. 2402, 1930; L. Vegard and A. Refsum, *Norske Vid. Akad. Skr. Oslo*, 2, 1927.

[18] J. B. Richter, *Ueber die neueren Gegenstände der Chemie*, Breslau, **1**. 49, 1791; **2**. 97, 1792; **10**, 86, 1802; H. S. Riederer, *Journ. Amer. Chem. Soc.*, **25**. 907, 1903; E. H. Miller and H. Frank,

ib., **25**. 919, 1903 ; E. H. Miller and F. van Dyke Cruser, *ib.*, **27**. 116, 1905 ; F. Zambonini, *Gazz. Chim. Ital.*, **50**. ii, 128, 1920 ; W. T. Schaller, *Bull. U.S. Geol. Sur.*, 610, 1916 ; E. F. Smith and R. H. Bradbury, *Ber.*, **24**. 2930, 1891.

[19] J. J. Berzelius, *Pogg. Ann.*, **6**. 384, 1826 ; A. Moberg, *De chloreto chromio*, Helsinfors, 1853 ; *De oxydochromoso*, Helsingfors, 1847 ; *Journ. prakt. Chem.*, (1), **29**. 173, 1843 ; (1), **43**. 125, 1848 ; (1), **44**. 332, 1848 ; H. Schultze, *Ueber die Darstellung krystallisirter Verbindungen, insbesondere über einige krystallisirte molybdänsaure und wolframsaure Salze*, Göttingen, 1862 ; S. Prakash and N. R. Dhar, *Journ. Indian Chem. Soc.*, **7**. 367, 1930.

[20] A. Lancien, *Bull. Sci. Pharm.*, **15**. 132, 1908 ; *Compt. Rend.*, **144**. 1434, 1907 ; B. Szilard, *ib.*, **145**. 480, 1907 ; C. F. Rammelsberg, *Pogg. Ann.*, **55**. 318, 1842 ; **56**. 125, 1842 ; **57**. 1, 1843 ; P. P. Pilipenko, *Vernadsky's Festschrift*, Moscow, 189, 1914 ; G. Carrobbi, *Rend. Accad. Napoli*, (3), **33**. 53, 1927.

[21] E. Marckwald, *Ueber die Molybdate des Kobalts, Nickels, Mangans, Eisens, Aluminiums, und Chroms*, Berlin, 1895 ; H. Schultze, *Ueber die Darstellung krystallisirter Verbindungen, insbesondere über einige krystallisirte molybdänsaure und wolframsaure Salze*, Göttingen, 1862 ; H. Struve, *Bull. Acad. St. Petersburg*, (2), **12**. 142, 1854 ; *Journ. prakt. Chem.*, (1), **61**. 453, 1854 ; J. B. Richter, *Ueber die neueren Gegenstände der Chemie*, Breslau, **1**. 49, 1791 ; **2**. 97, 1792 ; **10**. 86, 1802 ; A. Coloriano, *Bull. Soc. Chim.*, (2), **50**. 451, 1888 ; E. Péchard, *Compt. Rend.*, **125**. 31, 1897 ; O. Allemann, *Ueber Permanganmolybdate*, Bern, 1904 ; C. Friedheim and O. Allemann, *Mitt. Naturf. Ges. Bern*, 23, 48, 1904 ; M. Samelson, *Ueber Permanganmolybdate*, Leipzig, 1900 ; C. Friedheim and M. Samelson, *Zeit. anorg. Chem.*, **24**. 67, 1900 ; A. Rosenheim and H. Itzig, *ib.*, **16**. 81, 1898 ; A. Rosenheim, *ib.*, **96**. 139, 1916 ; F. Zambonini and V. Caglioti, *Atti Accad. Napoli*, **33**. 181, 1927 ; *Gazz. Chim. Ital.*, **59**. 400, 1929 ; R. D. Hall, *Journ. Amer. Chem. Soc.*, **29**. 692, 1907 ; W. Jander, *Zeit. anorg. Chem.*, **190**. 397, 1930 ; **191**. 171, 1930 ; **192**. 286, 295, 1930.

[22] E. Steinacker, *Ueber einige Molybdänverbindungen*, Göttingen, 1861 ; E. Marckwald, *Ueber die Molybdate des Kobalts, Nickels, Mangans, Eisens, Aluminiums, und Chroms*, Berlin, 1895 ; H. Schultze, *Ueber die Darstellung krystallisirter Verbindungen insbesondere über einige krystallisirte molybdänsaure und wolframsaure Salze*, Göttingen, 1862 ; G. Carobbi, *Rend. Accad. Napoli*, (3), **33**. 53, 1927 ; R. D. Hall, *Journ. Amer. Chem. Soc.*, **29**. 642, 1907 ; E. S. Simpson, *Journ. Roy. Soc. West. Australia*, **12**. 57, 1927 ; H. Struve, *Bull. Acad. St. Petersburg*, (2), **12**. 142, 1854 ; *Journ. prakt. Chem.*, (1), **61**. 453, 1854 ; C. W. Scheele, *Svenska Akad. Handl.*, **39**. 247, 1778 ; **40**. 238, 1779 ; W. T. Schaller, *Zeit. Kryst.*, **44**. 9, 1907 ; *Amer. Journ. Science*, (4), **28**. 297, 1907 ; P. P. Pilipenko, *Vernadsky's Festschrift*, Moscow, 189, 1914 ; C. Bärwald, *Beiträge zur Kenntnis des Molybdäns*, Berlin, 1885 ; G. Tammann, *Zeit. anorg. Chem.*, **149**. 21, 1925 ; S. Prakash and N. R. Dhar, *Journ. Indian Chem. Soc.*, **6**. 391, 587, 1929 ; **7**. 367, 1930.

[23] H. Schultze, *Ueber die Darstellung krystallisirter Verbindungen, insbesondere über einige krystallisirte molybdänsaure und wolframsaure Salze*, Göttingen, 1862 ; E. Marckwald, *Ueber die Molybdate des Kobalts, Nickels, Mangans, Eisens, Aluminiums, und Chroms*, Berlin, 1895 ; A. Coloriano, *Bull. Soc. Chim.*, (2), **50**. 451, 1888 ; J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817 ; *Pogg. Ann.*, **4**. 153, 1825 ; **6**. 331, 1826 ; **7**. 261, 1826 ; *Ann. Chim. Phys.*, (2), **17**. 5, 1821 ; F. de Carli, *Atti Accad. Lincei*, (6), **11**. 533, 1925 ; B. K. Paul and P. V. Sarkar, *Ann. Chim. Phys.*, (10), **5**. 199, 1926 ; F. L. Sonnenschein, *Journ. prakt. Chem.*, (1), **53**. 339, 1851 ; N. S. Kurnakoff, *Chem. Ztg.*, **14**. 113, 1900 ; C. Friedheim and F. Keller, *Ber.*, **39**. 4301, 1906 ; E. F. Smith and R. H. Bradbury, *ib.*, **24**. 2930, 1891 ; S. H. C. Briggs, *Journ. Chem. Soc.*, **85**. 672, 1904 ; W. Haidinger, *Jahrb. geol. Reichsanst. Wien*, **7**. 196, 1856 ; C. von Hauer, *ib.*, **7**. 196, 1856 ; J. von Jokély, *ib.*, **8**. 35, 1857 ; G. C. Laube, *ib.*, **14**. 303, 1863 ; R. D. Hall, *Journ. Amer. Chem. Soc.*, **29**. 692, 1907 ; P. R. Ray and S. N. Maulik, *Journ. Indian Chem. Soc.*, **7**. 607, 1930.

[24] J. B. Richter, *Ueber die neueren Gegenstände der Chemie*, Breslau, **1**. 49, 1791 ; **2**. 97, 1792 ; **10**. 86, 1802 ; C. Hatchett, *Phil. Trans.*, **95**. 323, 1795 ; H. Schultze, *Ueber die Darstellung krystallisirter Verbindungen ; insbesondere über einige krystallisirte molybdänsaure und wolframsaure Salze*, Göttingen, 1862 ; *Liebig's Ann.*, **126**. 49, 1863 ; E. Marckwald, *Ueber die Molybdate des Kobalts, Nickels, Mangans, Eisens, Aluminiums, und Chroms*, Berlin, 1895 ; S. H. C. Briggs, *Journ. Chem. Soc.*, **85**. 672, 1904 ; F. L. Sonnenschein, *Journ. prakt. Chem.*, (1), **53**. 339, 1851 ; G. L. Clark, *Amer. Journ. Science*, (5), **7**. 1, 1924 ; F. de Carli, *Atti Accad. Lincei*, (6), **11**. 533, 1925 ; W. Jander, *Zeit. anorg. Chem.*, **191**. 171, 1930 ; **192**. 286, 295, 1930.

[25] O. W. Gibbs, *Proc. Amer. Acad.*, **29**. 257, 1894 ; *Amer. Journ. Science*, (3), **14**. 62, 1877 ; *Amer. Chem. Journ.*, **17**. 80, 1895 ; *Ber.*, **10**. 1385, 1877 ; A. Rosenheim, *ib.*, **24**. 2397, 1891.

§ 12. The Di-, Para-, and Tri-Molybdates

L. F. Svanberg and H. Struve [1] found that the mother-liquor obtained in the preparation of ammonium molybdate, furnishes on evaporation crystals of **ammonium dimolybdate,** $(NH_4)_2O.2MoO_3$, or $(NH_4)_2Mo_2O_7$, or $NH_4O.MoO_2.O.MoO_2.ONH_4$. A. Rosenheim gave 0·530 to 0·539 for the transport number. F. Mauro prepared the monohydrate by evaporating a soln. of ammonium dioxytetrafluoride in ammonia. The colourless crystals appear to be monoclinic prisms, and, according to A. Scacchi, have the axial ratios $a : b : c = 0{\cdot}9663 : 1 : 0{\cdot}9450$, $\beta = 107^\circ 12'$. There are also triclinic plates. F. Mauro found that the crystals become turbid in air; and at 100°, begin to lose weight, ultimately forming, at higher temp., molybdenum trioxide. A. Classen prepared white, deliquescent crystals of **tetraethylammonium dimolybdate,** $\{N(C_2H_5)_4\}Mo_2O_7.3H_2O$.

F. Ephraim and M. Brand treated a soln. of 30 grms. of lithium molybdate with 42·3 c.c. of hydrochloric acid of sp. gr. 1·07, and obtained aggregates of needle-like crystals of **lithium dimolybdate,** $Li_2Mo_2O_7.5H_2O$, which at 120° lost one-third of their water of crystallization, and dissolved in water more readily than the trimolybdate. F. Hoermann found the dimolybdate has an incongruous m.p. at 532°, Fig. 13. L. F. Svanberg and H. Struve, and F. Ullik obtained what they regarded as **sodium dimolybdate,** $Na_2O.2MoO_3$, by fusing the required proportions of sodium carbonate or nitrate and molybdenum trioxide. The white mass dissolves in water, and the soln. yields small needles of what L. F. Svanberg and H. Struve regarded as the *monohydrate*, and F. Ullik, the anhydrous salt. E. Groschuff obtained the salt by melting equimolar parts of normal sodium molybdate and molybdenum trioxide. The salt melts at a dull red-heat to an oily liquid which crystallizes on cooling. F. Hoermann gave 612° for the m.p., Fig. 14. The salt is sparingly soluble in cold water but more soluble in hot water. J. J. Berzelius, F. Ullik, and L. F. Svanberg and H. Struve prepared what has been called **potassium dimolybdate** in an analogous way. M. Amadori's thermal analysis shows that potassium dimolybdate can exist. G. Canneri found that the alkali molybdates are reduced by hydrogen in accord with $R_2Mo_2O_7 + H_2 = MoO_2 R_2MoO_4 + H_2O$; reduction by tin furnishes a molybdenum blue; and electrolytic reduction gives compounds analogous with the tungsten bronzes. F. Ephraim and H. Herschfinkel obtained **rubidium dimolybdate,** $Rb_2M_2O_7.2H_2O$, by boiling a soln. of a mol of rubidium carbonate and 2 mols of molybdenum trioxide, and adding nitric acid of sp. gr. 1·20, drop by drop, to the filtered liquid until the precipitate first formed dissolves. The liquid furnishes crystals which are freely soluble in water. G. Wempe obtained this salt, $Rb_2Mo_2O_7.2\frac{1}{2}H_2O$, by evaporating the trimolybdate on a glass plate at 30° to 35°—he gave for it the formula $Rb_2MoO_4.Rb_2Mo_3O_{10}.5H_2O$.

A. Péchard reported that **silver dimolybdate,** $Ag_2Mo_2O_7$, is formed when silver permolybdate is melted. A. Junius obtained it by the action of a hot soln. of silver sulphate on a hot soln. of potassium pentamolybdate; and by the action of sodium paramolybdate on a soln. of silver nitrate. The powder consists of acicular crystals which are sparingly soluble in water, soluble in a soln. of potassium cyanide, and are decomposed by potash-lye with the precipitation of silver oxide. A. Atterberg obtained **beryllium dimolybdate,** $BeO.2MoO_3.3H_2O$, by fusing an eq. mixture of beryllic and molybdenum trioxide, extracting the mass with water, and evaporating the soln. over sulphuric acid. E. Marckwald reported **cobaltous dimolybdate,** $CoO.2MoO_3.6\frac{1}{2}H_2O$, to be formed by evaporating in the cold the soln. remaining after the precipitation of cobalt molybdate from a mixed soln. of sodium dimolybdate and cobaltous chloride. The brown needles form the *dihydrate*, $CoO.2MoO_3.2H_2O$, when heated to 100°.

By analogy with A. Laurent's [2] term paratungstates, a group of polymolybdates were designated **paramolybdates.** Owing to the difficulties involved in the preparation of the pure salts, and to the early difficulties attending the analysis of these salts, the formulæ assigned to them exhibit considerable deviations in the ratios $R_2O : MoO_3 : H_2O$—they include L. F. Svanberg and H. Struve's 4 : 9 : 6 for the potassium salt; F. E. Zenker's 4 : 9 : 28, and J. G. Gentele's 1 : 2 : 7 for the sodium salt; and L. F. Svanberg and H. Struve's and N. J. Berlin's 2 : 5 : 3, W. Delffs' and J. C. G. de Marignac's 1 : 2 : 1, and R. J. Maly's 1 : 4 : 2. W. Lotz showed that the best representative analysis is $3R_2O.7MoO_3.nH_2O$, and this formula, for example, very well represents the analyses of the ammonium salt by L. F. Svanberg and H. Struve, M. Delafontaine, F. Ullik, and A. Werncke.

A. Junius observed that with bases of higher mol. wt., *e.g.* the barium salt, the analyses agree better with the formula $5R_2O.12MoO_3.nH_2O$, and this is in harmony with the analysis of P. Klason and the observations of J. Sand and F. Eisenlohr on the $H^{\cdot}$-ion concentration when soln. of ammonium paramolybdate are titrated with alkali hydroxide. This is in agreement with the observations of A. Rosenheim and co-workers. Attempts have been made to find what proportion of the water is constitutional, and what proportion is water of crystallization, by measuring the loss of weight while the salt is gently heated at a given temp. in a current of carbon dioxide. The isothermal dehydration curves show breaks where there is a change in the properties of the salt. In harmony with the heteropoly salts like the silicododecatungstates, $R_8[Si(W_2O_7)_6]$, the phosphododecatungstates, $R_7[P(W_2O_7)_6]$, the phosphododecamolybdates, $R_7[P(Mo_2O_7)_6]$, the metatungstates, $R_6H_4[H_2(W_2O_7)_6]$, and the view that the so-called tetramolybdates are $R_6H_4[H_2(Mo_2O_7)_6]$, and the octomolybdates, $R_3H_7[H_2(Mo_2O_7)_6]$, A. Rosenheim represented the paramolybdates by the formula $R_5H_5[H_2(Mo_2O_7)_6]$. So that the tetra-, octo-, and para-molybdates are salts of the hypothetical acid $H_{10}[H_2(Mo_2O_7)_6]$. The dimolybdates are considered to be salts of the hypothetical acid $H_{10}[H_2(MoO_4)_6]$, namely $R_6H_4[H_2(MoO_4)_6]$; whilst the paramolybdates have five of the ten hydrogen atoms replaced to form $R_5H_5[H_2(MoO_4)_6]$; and the trimolybdates have four atoms of hydrogen displaced to form $R_4H_6[H_2(MoO_4)_6]$. To summarize,

Hexa-molybdates	Dimolybdates, or Tetrahydrohexamolybdates	$R_6H_4[H_2(MoO_4)_6]$
	Paramolybdates, or Pentahydrohexamolybdates	$R_5H_5[H_2(MoO_4)_6]$
	Trimolybdates, or Hexahydrohexamolybdates	$R_4H_6[H_2(MoO_4)_6]$
Dodeca-molybdates	Tetramolybdates, or Tetrahydrododecamolybdates	$R_6H_4[H_2(Mo_2O_7)_6]$
	Hexamolybdates, or Hexahydrododecamolybdates	$R_4H_6[H_2(Mo_2O_7)_6]$
	Octomolybdates, or Heptahydrododecamolybdates	$R_3H_7[H_2(Mo_2O_7)_6]$

The two hydrogen atoms in the nucleus can be replaced by a bivalent metal—copper, calcium, magnesium, manganese, nickel, or cobalt—to form salts of the hypothetical acid:

$$H_{10}[M''(MoO_4)_6].nH_2O.$$

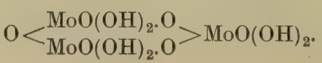
There is also an isomorphous series of salts with a tervalent metal—aluminium, chromium, iron, cobalt, or rhodium—in the nucleus:

$$R_3H_6[M'''(MoO_4)_6].7H_2O.$$

There is a salt with a quadrivalent metal in the nucleus—*viz.* tin—represented by

$$(NH_4)_8[Sn''''(Mo_2O_7)_6].20H_2O.$$

Other hypotheses can be devised. H. Copaux suggested that the polymolybdates are derived from a hypothetical orthomolybdic acid, H_6MoO_6, by substituting the oxygen atoms one by one with the eq. Mo_2O_7-radicle. This makes the $3R_2O.7MoO_3.nH_2O$ formula for the paramolybdates assume the form $R_6[Mo(Mo_2O_7)_3O_3]$. S. Posternak obtained what he regarded as an anhydrous paramolybdate which he supposed to be $(NH_4O)_3MoO(O.MoO_2)_5O.MoO(ONH_4)_3$, and he also obtained what he regarded as $(NH_4O)_3MoO(O.MoO_2)_5O.MoO_2(OH)$, and $NH_4O(OH)_2MoO(O : MoO_2)_5O.MoO_2(OH).H_2O$. He also obtained ammonium salts of the complex $(RO)_3MoO(O.MoO_2)mO.Mo(OR)_3.nH_2O$. These condensation products reach their limit with the tridecamolybdate. He added that the classification of the molybdates into ortho-, meta-, and para-molybdates is unsatisfactory; and that there are only two groups of molybdates (i) the R_6-polymolybdates in which the ortho- and para-salts are only particular cases; and (ii), the R_4-polymolybdates formed by the hydrolytic rupture of the R_6-salts. L. Forsén regarded the molybdates as derivatives of the two acids: molybdic acid, $H_6Mo_2O_{12}$; and metamolybdic acid, $H_{12}Mo_2O_{12}$. The former is represented by



$$O{<}\begin{matrix}MoO(OH)_2.O\\MoO(OH)_2.O\end{matrix}{>}MoO(OH)_2.$$

Anhydrides like $H_4Mo_3O_{11}$, and $H_2Mo_3O_{10}$, can be formed. He regarded metamolybdic acid as a condensation product of four molecules of molybdic acid so as to form the complex $H_6[Mo_{12}O_{42}H_6]$; and obtained it by warming molybdic acid with hydrochloric acid and a little nitric acid.

A. Travers and L. Malaprade considered that the acid molybdates are derivatives of tetramolybdic and normal molybdic acids $H_2[4MoO_3.O]$ and $H_2[MoO_4]$. The trimolybdates and paramolybdates are derived from the ions $[3MoO_3,O]$ and $[7MoO_3,3O]$, respectively. These ions are considered to exist in equilibrium with the normal and tetramolybdic ions. Ammonium paramolybdate appears to have the composition $12MoO_3.4(NH_4)_2O$, but is probably composed of mixed crystals of tri- and para-molybdate in equilibrium with a mother-liquor of the same composition. The correct formula for sodium paramolybdate is taken to be $3Na_2O.7MoO_3.22H_2O$, and the ammonium salt, $5(NH_4)_2O.12MoO_3.7H_2O$, consists of an isomorphous mixture of true paramolybdate, $3(NH_4)_2O.7MoO_3$, with the trimolybdate, $3(NH_4)_2O.6MoO_3$, and the composition remains constant on recrystallization because the crystals are deposited from a mother-liquor of the same composition.

L. F. Svanberg and H. Struve prepared crystals of **ammonium paramolybdate,** or ordinary commercial ammonium molybdate, by the evaporation of a soln. of molybdic acid in aq. ammonia. Analyses by L. F. Svanberg and H. Struve, W. Delffs, J. C. G. de Marignac, H. Rose, C. F. Rammelsberg, W. Lotz, J. Terwelp, F. Westphal, M. Delafontaine, F. Ullik, and A. Werncke are in accord with the *tetrahydrate*, $3(NH_4)_2O.7MoO_3.4H_2O$, although, for reasons indicated above, other formulæ have been given which represent the analyses nearly as well. Actually J. J. Berzelius called it a diacid salt; L. F. Svanberg and H. Struve represented it by $2(NH_4)_2O.5MoO_3.3H_2O$; J. C. G. de Marignac, and W. Delffs, by $(NH_4)HMoO_4$; and P. Klason regarded it as $5NH_3.6MoO_3.6H_2O$, a complex of $(NH_4)_3H_3Mo_3O_{12}$ and $(NH_4)_2H_4Mo_3O_{12}$. The competing formulæ are $5(NH_4)_2O.12MoO_3.7H_2O$, favoured by A. Junius, and J. Sand and F. Eisenlohr; and $(NH_4)_5H_5[H_2(MoO_4)_6]$, favoured by A. Rosenheim and co-workers. According to C. F. Rammelsberg, the spontaneous evaporation of the mother-liquor from the tetrahydrate yields the *dodecahydrate*, in small monoclinic crystals with the axial ratios $a:b:c=0·4977:1:0·7461$, and $\beta=106° 35'$. It is more soluble than the tetrahydrate; the cooling of the aq. soln. yields the tetrahydrate. The colourless crystals of the tetrahydrate obtained by L. F. Svanberg and H. Struve were six-sided prisms; and G. vom Rath said that the monoclinic prisms have the axial ratios $a:b:c=0·6297:1:1·2936$, and $\beta=91° 21'$; and the (010)-cleavage is complete. H. Steinmetz discussed the crystals of this salt. M. Delafontaine said that the crystals of the *tetrahydrate* have a bluish tinge, due, according to N. J. Berlin, to the presence of a trace of blue molybdenum oxide. Observations on the crystals were also made by W. Haidinger, J. C. G. de Marignac, and C. F. Rammelsberg. N. J. Berlin said that when the salt is heated to redness, it loses water, nitrogen, and ammonia, and leaves behind a brown oxide or else, if air be present, molybdenum trioxide. F. Westphal said that half the water is lost after the salt has stood two months over conc. sulphuric acid or phosphorus pentoxide. P. Klason found that no water is lost under these conditions. F. Westphal observed that at 90°, all the water is given off; at temp. up to 150°, ammonia is gradually given off; over 190°, the evolution of ammonia is accompanied by a darkening of the mass; and at 230°, molybdenum trioxide remains. N. J. Berlin thought that in aq. soln. the trimolybdate is formed. If the freshly-prepared, cold, sat. aq. soln. is dialyzed, dimolybdate escapes, and an acidic liquor remains; if allowed to stand a long time, di- and tri-molybdates are formed: $3\{(NH_4)_2O.7MoO_3\}=(NH_4)_2O.3MoO_3+2(NH_4)_2Mo_2O_7$. If the aq. soln. is heated, some ammonia escapes; and if the soln. is heated in a sealed tube, it is supposed the reaction is that symbolized by $3\{(NH_4)_2O.7MoO_3\}=(NH_4)_2O.4Mo_3O+2(NH_4)_2O.3MoO_3$. On mixing the soln. with other chlorides—*e.g.* those of potassium, calcium, strontium, barium, or magnesium—an isomorphous mixture $m\{3(NH_4)_2O.7MoO_3\}.n\{3R_2O.7MoO_3\}$ is formed. J. N. Rakshit studied the contraction which occurs when the salt is dissolved in water. P. Klason observed that a mixture of 23·22 grms. of water and 3·5846 grms. of salt has a f.p. $-0·625°$, and one of 23·91 grms. of water and 4·1041 grms. of salt, a f.p. of $-0·665°$. This corresponds with the mol. wt. 452 and 472 respectively. A soln. of 18·9 grms. of water and 4·4281 grms. of salt has a b.p. 100·35°, and a soln. of 16·9 grms. of water and 5·4519 grms. of salt, a b.p. of 100·42°. The corresponding mol. wts. are 348 and 399. E. Darmois and J. Périn found that the mol. wt. of the salt is normal when calculated from the f.p. of its soln. in decahydrated sodium sulphate. A. Rosenheim's formula for the salt requires a mol. wt. of 1057. J. Terwelp gave for the eq. conductivity, λ mhos, of an eq. of the salt, $\frac{1}{6}\{(NH_4)_6Mo_7O_{24}.4H_2O\}$, in v litres of water at 25° :

v . .	32	64	128	256	512	1024
λ . .	105·5	119·7	131·5	142·2	154·4	170·9

The aq. soln. has an acidic reaction. J. Sand and F. Eisenlohr said that the salt —represented by A. Junius' formula $(NH_4)_{10}Mo_{12}O_4$—is slightly hydrolyzed so that, at 25°, the $H^{\cdot}$-ion conc. of a $0·01M$-soln. is $1·17\times10^{-4}$ corresponding with a 0·19 per cent. hydrolysis : $Mo_{12}O_{41}{}^{X}+3H_2O\rightleftharpoons2Mo_6O_{22}{}^{VIII}+6H^{\cdot}$. In the progressive hydrolysis of the salt the complex salt $(NH_4)_8Mo_6O_{22}$ is formed before the simple molybdate $(NH_4)_2MoO_4$. There are also indications that a second polymolybdate ion is formed. They said that the original salt ionizes normally : $(NH_4)_{10}Mo_{12}O_{41}\rightleftharpoons10NH_4{}^{\cdot}+Mo_{12}O_{41}{}^{X}$; and on progressive neutralization, there are two possibilities : (i) there is hydrolytic equilibrium, $Mo_{12}O_{41}{}^{X}+7H_2O\rightleftharpoons12MoO_4''+14H^{\cdot}$, so that the addition of sodium hydroxide will remove the $H^{\cdot}$-ions and in all stages of the process there will be equilibrium between the $Mo_{12}O_{41}{}^{X}$,MoO_4'', and the $H^{\cdot}$-ions ; or (ii) one or more polymolybdates may be formed. The position of the break in the curve representing the $H^{\cdot}$-ion conc. and the amount of sodium hydroxide added to the soln. corresponds better with the assumption that the reaction is : $Mo_{12}O_{41}{}^{X}+6OH'=4Mo_3O_{11}{}^{IV}+3H_2O$. S. Dushman found that the rate at which iodine is liberated from a mixture of potassium iodide and iodate in acidic soln. is proportional to the conc. of the iodate ion, and to the square of the conc. of the iodine and hydrogen ions, and J. Sand and F. Eisenlohr utilized the reaction to measure the $H^{\cdot}$-ion conc. in the liberation of iodine from mixtures of potassium iodide, iodate, and ammonium molybdate. Constant values are not obtained for $K=[Mo_6O_{22}{}^{VIII}]^2[H^{\cdot}]^6/[Mo_{12}O_{41}{}^{X}]$ on the assumption that $Mo_3O_{11}{}^{IV}$-ions are present, but constant values are obtained on the assumption that the ions are $Mo_6O_{22}{}^{VIII}$, and at 25°, $K=3·80\times10^{-31}$. B. Glasmann represented the end-products of the hydrolysis : $3(NH_4)_6Mo_7O_{24}+12H_2O=9(NH_4)_2MoO_4+12H_2MoO_4$, and the molybdic acid so produced reacts with the mixture of potassium iodide and iodate : $20KI+4KIO_3+12H_2MoO_4=12K_2MoO_4+12I_2+12H_2O$. S. E. Moody represented the reaction : $3(NH_4)_6Mo_7O_{24}.4H_2O=18NH_3+21H_2MoO_4$; followed by $21H_2MoO_4+35KI+7KIO_5=21K_2MoO_4+21I_2+21H_2O$. A. Junius observed that when an aq. soln. of ammonium paramolybdate is electrolyzed, ammonium tetramolybdate collects at the anode. A. Rosenheim prepared the paramolybdates of ethylamine, aniline, pyridine, and guanidine, of the type $5(CN_3H_6)_2O.12MoO_3.4H_2O$. For **hydroxylamine paramolybdates,** *vide supra.*

A. Rosenheim prepared needle-like crystals of **lithium paramolybdate,** $3Li_2O.7MoO_3.12H_2O$, by evaporating a soln. of a mol of lithium carbonate and 2 mols of molybdic acid, and allowing it to crystallize over phosphorus pentoxide. In addition to this *dodecahydrate,* F. Ephraim and M. Brand reported that the *octocosihydrate* is obtained by evaporating in the cold a soln. of 7 mols of lithium molybdate and 8 mols of nitric acid. The needle-like crystals are easily soluble in cold or hot water. M. Delafontaine, F. E. Zenker, and J. G. Gentele prepared

sodium paramolybdate, $3Na_2O.7MoO_3.22H_2O$, by treating with nitric acid a soln. of molybdic acid in one of sodium hydroxide or carbonate until the first precipitate dissolves, and the soln. has an acid reaction. The liquid deposits the salt in crystals. F. Ullik, and A. Rosenheim obtained it from a soln. of the calculated quantity of molybdic acid or an acid molybdate and the calculated proportion of sodium carbonate ; and F. Mauro obtained it from a soln. of molybdic acid in one of borax —perborate and trimolybdate are also formed. A. Junius obtained the paramolybdate by electrolyzing a soln. of 50 to 60 grms. of the normal salt in 350 c.c. of water, in a compartment cell, using a current of 4 amps. and 8 to 10 volts for 60 to 75 minutes. The anode liquor is allowed to crystallize. A. Lottermoser made a cell with a soln. of sodium molybdate in the inner anode compartment, $0 \cdot 1N$-NaOH in the outer cathode compartment, a platinum cylinder formed the anode. On electrolysis, sodium paramolybdate was found in the interior cell. The salt was analyzed by M. Delafontaine, F. Ullik, J. G. Gentele, and F. E. Zenker, and the formula approximates to $3Na_2O.7MoO_3.22H_2O$, or $5Na_2O.12MoO_3.36H_2O$, or, according to A. Rosenheim, $Na_5H_5[H_2(MoO_4)_6].15\frac{1}{2}H_2O$. F. Westphal regarded it as an *icosihydrate*, $3Na_2O.7MoO_3.20H_2O$. G. Wempe obtained what he regarded as $5Na_2O.12MoO_3.nH_2O$, with n=8, 20, 36, and 44. The colourless, monoclinic prisms were found by F. E. Zenker to have the axial ratios $a:b:c = 2 \cdot 0923 : 1 : 2 \cdot 0237$, and $\beta = 103° 25'$. The (100)-cleavage is incomplete. According to F. E. Zenker, J. G. Gentele, M. Delafontaine, and F. Ullik, the crystals are stable in air only at a low temp. ; at room temp., it effloresces giving off 8 mols. of water ; over sulphuric acid, 11 mols., and at 100°, 21 mols. F. Ullik said that the last mol. is expelled at 120°–130° ; M. Delafontaine said at 200°. H. Copaux found that one mol. remains at 100° ; 0·5 mol. at 150° ; and all is expelled at 200° ; and A. Rosenheim, that 15·5 mols. are expelled at 60°, and 18 mols. at 100°. The salt readily fuses in its water of crystallization. The dehydrated salt readily fuses—L. Ott gave 700° for the m.p.—and it is no longer completely soluble in water. When the salt which has been fused is treated with water it leaves needle-like crystals, which, according to E. Groschuff, are those of the dimolybdate. The f.p. curve of E. Groschuff, Fig. 14, shows that the fused paramolybdate is a mixture of molybdenum trioxide and sodium dimolybdate ; it is also doubtful if the dehydrated paramolybdate is a chemical individual. According to A. Rosenheim, 100 grms. of water at 30° dissolve 117·7 grms. of salt calculated as $5Na_2O.12MoO_3$, or 100 grms. of soln. contain 56·06 grms. The solubility is greater in hot soln., and hydrated paramolybdate is deposited as the soln. cools, but warm conc. soln. of the paramolybdate when boiled deposit trimolybdate. The addition of sodium carbonate to a soln. of paramolybdate forms the monomolybdate. A. Rosenheim gave for the electrical conductivity, λ mhos, of a soln. of one-tenth of a mol of $5Na_2O.12MoO_3.36H_2O$ in v litres at 25°,

v . .	16	32	64	128	256	512	1024
λ . .	89·0	99·8	108·7	116·9	124·8	135·1	146·1

L. Ott said that the molten salt dissolves iron, and when the cold mass is treated with water, ferric oxide remains undissolved. F. E. Brown and J. E. Snyder observed no action with anhydrous ammonium molybdate and boiling vanadium oxytrichloride.

L. F. Svanberg and H. Struve obtained **potassium paramolybdate,** $3K_2O.7MoO_3.4H_2O$, or may be $5K_2O.12MoO_3.7$ or $8H_2O$, by mixing a soln. of molybdic acid in potassium carbonate, drop by drop, with hydrochloric or nitric acid until a permanent turbidity is produced ; the soln. soon deposits crystals of the salt. M. Delafontaine obtained the salt by evaporating to dryness a soln. of molybdic acid in an excess of potassium carbonate, digesting the mass with water, and allowing the soln. to crystallize. A. Rosenheim fused a mixture of equimolar parts of molybdenum trioxide and potassium carbonate, added nitric acid to the aq. soln. until the liquid was neutral to litmus, and allowed the soln.

to crystallize. A. Junius electrolyzed in a diaphragm cell a soln. of 45 grms. of potassium molybdate in 350 c.c. of water for half an hour using a current of 1 to 2 amp. and 8 volts, and allowing the anode liquor to crystallize. If the electrolysis be continued too long, or if the current strength be too high, potassium trimolybdate is formed. According to J. C. G. de Marignac, the six-sided prisms are monoclinic with the axial ratios $a : b : c = 0{\cdot}621 : 1 : 0{\cdot}291$, and $\beta = 90^\circ\ 25'$, and they are isomorphous with the corresponding ammonium salt. According to L. F. Svanberg and H. Struve, and M. Delafontaine, the salt is sparingly soluble in cold water and is thereby decomposed into the normal and trimolybdate ; it loses its combined water when heated, and melts at a red-heat forming a yellow glass. The salt is stable only when quite dry, or when confined under its mother-liquor.

M. Delafontaine reported **rubidium paramolybdate,** $3Rb_2O.7MoO_3.4H_2O$—or, according to G. Wempe, $5Rb_2O.12MoO_3.nH_2O$—to be formed by melting rubidium carbonate with an excess of molybdenum trioxide, dissolving the cold mass in hot water, and cooling the soln. F. Ephraim and H. Herschfinkel used a similar process. W. Muthmann and W. Nagel obtained the paramolybdate by fusing a mol of rubidium carbonate with 3 mols of molybdenum trioxide ; dissolving the cold mass in water ; and crystallizing. F. Ephraim and H. Herschfinkel added that the crystals lose 2 mols. of water at 120°, and all the water is expelled at 180°. The six-sided prisms are said to be isomorphous with the ammonium salt and to be sparingly soluble in cold, but more soluble in hot water. It can be crystallized unchanged from its aq. soln. G. Wempe said that 100 c.c. of the aq. soln. at 24° contain 1·941 grms. of the salt. M. Delafontaine gave the formula $Rb_2O.3MoO_3.2H_2O$, using a wrong value for the at. wt. of rubidium. F. Ephraim and H. Herschfinkel added that the mother-liquor furnishes acicular crystals of $4Rb_2O.5MoO_3.12H_2O$, or $5Rb_2O.7MoO_3.14H_2O$, but the individuality of the product was not established. G. Wemple obtained **rubidium hydroparamolybdate,** $2Rb_2O.H_2O.7MoO_3.5H_2O$, from a soln. of molybdic acid saturated with rubidium carbonate. A. Rosenheim prepared **cæsium paramolybdate,** $3Cs_2O.7MoO_3,nH_2O$, or $5Cs_2O.12MoO_3.11H_2O$, by evaporating the soln. obtained by boiling a soln. of 2 mols of molybdic acid with a mol of cæsium carbonate. F. Ephraim and H. Herschfinkel using analogous proportions of molybdic acid and cæsium hydroxide obtained the 1 : 5 : 5-molybdate, not the paramolybdate.

F. Westphal prepared white needles of **ammonium calcium paramolybdate,** according to A. Rosenheim, $(NH_4)_3CaH_5[H_2(MoO_3)_6].9H_2O$, by the action of ammonium paramolybdate on a soln. of calcium chloride. F. Westphal obtained a substance of the composition $2SrO.3MoO_3$, but it was probably a mixture of **strontium paramolybdate** (3 : 7) and monomolybdate 1 : 5. It was obtained as a white amorphous mass by mixing soln. of sodium dimolybdate and strontium chloride. L. F. Svanberg and H. Struve prepared **barium paramolybdate,** $3BaO.7MoO_3.9H_2O$, or $5BaO.12MoO_3.nH_2O$, by double decomposition between barium chloride and an alkali or ammonium paramolybdate. F. Westphal said that the air-dried precipitate is the *decosihydrate.* A. Junius, working with cold soln., said that the precipitate is the *dodecahydrate,* $3BaO.7MoO_3.12H_2O$, or $5BaO.12MoO_3.20H_2O$, and when boiled it forms the *hexahydrate,* $3BaO.7MoO_3.6H_2O$, or $5BaO.12MoO_3.10H_2O$. F. Westphal obtained **ammonium barium paramolybdate,** $3(NH_4)_2O.3BaO.14MoO_3.12H_2O$, by crystallization from a clear soln. of a mol of barium chloride and 10 mols of ammonium paramolybdate.

F. Ullik prepared **magnesium paramolybdate,** $3MgO.7MoO_3.20H_2O$, by spontaneously evaporating a soln. of the normal molybdate in nitric acid. The plates and prisms are stable in air ; they lose water at a red-heat ; and are soluble in cold water and still more soluble in hot water. E. Manassewitsch could not prepare **zinc paramolybdate ;** by treating a zinc salt soln. with sodium paramolybdate, a mixed precipitate was obtained, and with ammonium paramolybdate, **ammonium zinc paramolybdate,** $2(NH_4)_2O.ZnO.7MoO_3.15H_2O$, was obtained as a white, insoluble precipitate. A. Junius could not prepare cadmium paramolybdate by double decomposition; but E. Mannassewitsch obtained **ammonium cadmium paramolybdate,** $2(NH_4)_2O.CdO.12MoO_3.9H_2O$.

A. Junius prepared **thallous paramolybdate,** $3Tl_2O.7MoO_3$, or $5Tl_2O.12MoO_3$, as a yellow, microcrystalline precipitate, by adding to an excess of a hot soln. of thallous sulphate a hot soln. of sodium paramolybdate. The salt is sparingly soluble in water; but freely soluble in a soln. of alkali hydroxide or carbonate, or in mineral acids. The salt melts to a deep brown liquid at dull redness. H. Flemming reported two acid salts to be formed by double decomposition. The one, $8Tl_2O.11MoO_3$, is supposed to be a mixture of the normal and the paramolybdate; and the other, $3Tl_2O.8MoO_3$, nearly all paramolybdate. A. Cleve prepared crystals of **ytterbium paramolybdate,** $Yb_2O_3.7MoO_3.6H_2O$, by adding a soln. of ytterbium nitrate to a soln. of ammonium paramolybdate, and allowing the soln. to stand for some time, and drying the colourless crystals at 130°.

G. A. Barbieri prepared a series of rare-earth molybdates of the general formula $(NH_4)_6R_2'''Mo_{14}O_{48}.24H_2O$, or $(NH_4)_3R'''Mo_7O_{24}.12H_2O$. The salts can be regarded as complex paramolybdates. They all furnish triclinic crystals and are isomorphous. The crystallographic data are by E. Billows. The red, triclinic prisms of **ammonium cerous molybdate,** $(NH_4)_6Ce_2Mo_{14}O_{48}.24H_2O$, have the axial ratios $a:b:c=0{\cdot}3533:1:0{\cdot}3409$, and $\alpha=102°\ 22'$; $\beta=54°\ 30'$; and $\gamma=103°\ 4'$, are soluble in water; the white crystals of **ammonium lanthanous molybdate,** $(NH_4)_6La_2Mo_{14}O_{48}.24H_2O$, have a yellow tinge, and the axial ratios $a:b:c=0{\cdot}3502:1:0{\cdot}3416$, and $\alpha=102°\ 29'$, $\beta=54°\ 18'$, and $\gamma=103°\ 10'$. These two compounds readily form isomorphous mixtures. G. A. Barbieri, and E. Billows also described **ammonium neodymium molybdate,** $(NH_4)_6Nd_2Mo_{14}O_{48}.24H_2O$, with the axial ratios $a:b:c=0{\cdot}3492:1:0{\cdot}3385$, and $\alpha=102°\ 15'$, $\beta=54°\ 8'$, and $\gamma=103°\ 39'$; **ammonium praseodymium molybdate,** $(NH_4)_6Pr_2Mo_{14}O_{48}.24H_2O$, with $0{\cdot}3514:1:0{\cdot}3461$, and $\alpha=102°\ 11'$, $\beta=54°\ 15'$, and $\gamma=103°\ 44'\ 30''$; and **ammonium samarium molybdate,** $(NH_4)_6Sa_2Mo_{14}O_{48}.24H_2O$, with $0{\cdot}3611:1:0{\cdot}3330$, and $\alpha=54°\ 45'$, $\beta=54°\ 45'$, and $\gamma=102°\ 36'\ 30''$.

A. Lancien found that when uranium nitrate is added to an excess of ammonium paramolybdate, and the resulting precipitate is boiled with molybdic acid, **uranyl paramolybdate,** $3(UO_2).7MoO_3$, is obtained as an amorphous, yellow powder. It is soluble in all mineral acids, giving a greenish-yellow, fluorescent liquid; it is decomposed by excess of water, and reduced to green uranium molybdate, $U(MoO_4)_2$, by alcohol and by acetic acid. The effect of sunlight on the heptamolybdate is to darken its colour, and to render it no longer reducible by alcohol or completely soluble in nitric acid, owing to the formation of insoluble anhydrous uranium octomolybdate, $8MoO_3,UO_3$ and the hydrated compound, $8MoO_3,UO_3,13H_2O$, was also prepared.

For **manganese paramolybdates,** *vide supra,* the molybdates. E. Marckwald could not prepare cobaltous paramolybdate, but A. Carnot obtained what appeared to be **cobaltic pentamminoparamolybdate,** $Co_2O_3.7MoO_3.5NH_3.3H_2O$, by oxidizing an ammoniacal soln. of a cobaltous salt with hydrogen dioxide, adding ammonium paramolybdate, and then acidifying the liquor with acetic acid to precipitate the salt. This compound loses ammonia and water when heated. The reaction can be used as a test for cobalt salts. E. Marckwald obtained **ammonium cobaltous paramolybdate,** $3(NH_4)_2O.3CoO.7MoO_3,nH_2O$, or $5(NH_4)_2O.5CoO.24MoO_3.nH_2O$, from soln. of cobaltous chloride and ammonium paramolybdate evaporated over sulphuric acid. Dark red prisms are obtained. He also reported a hydrated series of, probably, mixtures of ammonium paramolybdate, and cobaltous paramolybdate $(3(NH_4)_2O.7MoO_3):(3CoO.7MoO_3)=5:7$; $2:3$; $3:5$; and $1:5$. **Sodium cobaltous paramolybdate,** $Na_2O.CoO{\cdot}7MoO_3.20H_2O$, was obtained by E. Marckwald from a mixture of eq. proportions of soln. of sodium dimolybdate and cobaltous chloride, and after filtering off the precipitated normal cobaltous molybdate, concentrating by heat. The dark red crystals are slowly soluble in cold water, and without decomposition; and dissolve without decomposition in hot water, but the hot soln. soon decomposes. E. Marckwald concentrated a soln. of a mol of sodium paramolybdate and cobaltous chloride in the cold over conc. sulphuric acid and obtained dark red, prismatic needles of the composition $3Na_2O.3CoO.14MoO_3.50H_2O$. The soln. in cold water is clear and does not become turbid when heated.

According to an observation of N. J. Berlin,[3] **ammonium trimolybdate,** $(NH_4)_2O.3MoO_3.nH_2O$, is formed during the spontaneous evaporation of a soln. of ammonium paramolybdate. F. Westphal, and L. Kämmerer obtained it by keeping a conc. soln. of that salt for a long time at ordinary temp.; and P. Klason, and G. Wempe, by treating a soln. of the paramolybdate with the calculated quantity of hydrochloric acid. N. J. Berlin considered the product to be a trihydrate; and L. Kämmerer, a monohydrate. The radiating masses of acicular crystals, or crystalline crusts, according to P. Klason, lose half their water when confined over phosphorus pentoxide. The salt dissolves sparingly in cold water, and freely in hot water, and it crystallizes slowly from the aq. soln. yielding an impure product.

M. Delafontaine reported **lithium trimolybdate,** $Li_2O.3MoO_3.8H_2O$, to be formed by boiling a soln. of the acid molybdate with lithium carbonate. The *octohydrate* furnishes tetrahedral crystals—monoclinic or triclinic. The salt is not decomposed by fused sodium carbonate. F. Ephraim and M. Brand obtained the *heptahydrate* by evaporating a sat. soln. of the tetramolybdate; the molybdic acid which first separates is filtered off, and on evaporation the liquid furnishes acicular crystals which lose 4 mols. of water at 100°, and 6 mols. at 145°. The salt is sparingly soluble in cold water but more soluble in hot water. G. Wempe obtained the *monohydrate* by evaporating a soln. of 4 mols of lithium molybdate and 6 mols of hydrochloric acid. He also reported a *tetrahydrate,* and one with rather more water. F. Hoermann found that lithium trimolybdate has an incongruent m.p. at 549°—Fig. 13.

L. F. Svanberg and H. Struve obtained **sodium trimolybdate,** $Na_2O.3MoO_3.7H_2O$, by treating a conc. soln. of molybdic acid and sodium carbonate with conc. nitric acid, drop by drop, and the strongly acid soln. gradually deposited acicular crystals of the *heptahydrate* when allowed to evaporate spontaneously. F. Ullik obtained the same salt by spontaneously evaporating a soln. of a mol of sodium carbonate, and 3 mols of molybdenum trioxide—H. Struve used sodium hydroxide instead of the carbonate. A. Rosenheim said that a soln. of the paramolybdate furnishes the trimolybdate when heated a long time; and A. Junius found that if the electrolysis, in the preparation of the paramolybdate, is continued a long time, the trimolybdate is formed. F. Ullik found that the salt melts at a red-heat, and solidifies to a crystalline mass. F. Hoermann, Fig. 14, found that the salt has an incongruent m.p. at 528°. E. Groschuff observed no sign of the formation of a trimolybdate on the f.p. curve, Fig. 14. This is in harmony with L. F. Svanberg and H. Struve's, and F. Ullik's observations that the salt is reduced to brown dioxide by hydrogen, or by zinc. F. Ullik observed that the acicular crystals of the heptahydrate lose about 6 mols. of water at 100°, or at 120°. F. Ullik found that 100 grms. of a soln. sat. at 20° contain 2·96 grms. of the anhydrous salt, and at 100°, 45·86 grms. A. Rosenheim found that at 30°, 100 grms. of a sat. soln. contain 13·68 grms. of $Na_2Mo_3O_8$. According to F. Ullik, a hot conc. soln. of the heptahydrate on a glass plate in dry air at room temp. forms amorphous *tetrahydrate.* It is easily and completely soluble in water. A. Junius reported the *henahydrate* to be precipitated when the anode liquor indicated above is treated with alcohol; he also obtained the *enneahydrate* in a similar way, and G. Wempe obtained the enneahydrate from the mother-liquor in the preparation of the tetramolybdate, and he also obtained *hemidodecatrihydrate* as a crystalline crust when preparing the tetramolybdate. G. Wempe gave for the eq. conductivity, λ, of an eq. of the salt in v litres of water at 20°,

v	10	20	40	80	160
λ tetrahydrate	64·7	72·5	80·0	80·0	96·6
λ hemidodecahydrate	63·7	75·2	85·6	95·2	105·9
λ enneahydrate	76·0	90·0	104·0	112·0	131·2

L. F. Svanberg and H. Struve, and G. Wempe prepared **potassium trimolybdate,** $K_2O.3MoO_3.3H_2O$, by stirring the paramolybdate for some days with cold water, and by treating a soln. of molybdic acid and potassium carbonate with nitric acid —H. Struve used potassium hydroxide. F. Ullik melted 2 mols of potassium carbonate with a mol of molybdenum trioxide; boiled the cold cake with water, and allowed the soln. to crystallize. As in the case of the sodium salt, A. Junius obtained it by the prolonged electrolysis of a soln. of potassium molybdate; and precipitating the anode liquid with alcohol. M. Amadori's thermal analysis shows that the trimolybdate can exist. G. Jander and A. Winkel found the salt to be stable in the range $[H^{\cdot}]=10^{-6\cdot2}$ to $10^{-4\cdot6}$, and gave 0·35 for the diffusion coeff. of the anion. G. Jander described the conditions of stability of the acid. F. Hoermann, Fig. 14, found that the salt melts at 571°. L. F. Svanberg and H. Struve, M. Delafontaine, F. Ullik, and G. Wempe found that the acicular crystals are stable in air; they lose water completely at 100°; they melt at a red-heat, and form a crystalline mass on cooling; when heated in hydrogen, molybdenum dioxide is formed; the dehydrated salt expels 16·82 per cent. of carbon dioxide from molten alkali carbonate; the salt is sparingly soluble in cold water, and more easily soluble in hot water—but less so than is the case with the sodium salt. G. Wempe gave for the conductivity, λ, of an eq. of the salt in v litres of water at 20°:

v	20	40	80	160	320
λ	91·8	104·4	124·0	136·6	153·6

W. Muthmann and W. Nagel melted a mol of rubidium carbonate with 3 mols of molybdenum trioxide, dissolved the white crystalline mass in water, and evaporated the soln. over sulphuric acid. White needles of the *monohydrate* of **rubidium trimolybdate,** $Rb_2O.3MoO_3.H_2O$, were formed. According to F. Ephraim and H. Herschfinkel, an aq. soln. of rubidium paramolybdate furnishes on evaporation a crop of crystals of 3:8:6-molybdate followed by the *hemitridecahydrate* of the trimolybdate. G. Wempe obtained the *trihydrate* by evaporating the aq. soln. on a glass plate; and if the soln. be evaporated on a glass plate at 30° to 35°, the dimolybdate is formed. W. Muthmann and W. Nagel could not prepare **cæsium trimolybdate,** $Cs_2O.3MoO_3.H_2O$, by the process used for the rubidium salt, but F. Ephraim and H. Herschfinkel obtained it as a white, amorphous mass, by evaporating the mother-liquor of the most acid cæsium salt. It is possible that what is here called the trimolybdate may be the 3 : 10 : 3-molybdate.

F. Ullik obtained **copper trimolybdate,** $CuO.3MoO_3.9H_2O$, from a boiling soln. of a mol. of copper carbonate and 4 mols of molybdic acid, and allowing the filtrate to evaporate spontaneously. The pale blue masses of needles are sparingly soluble in cold water and freely soluble in hot water. If an aq. soln. be evaporated on a glass plate, a greenish-blue gummy mass, $CuO.3MoO_3.6\frac{1}{2}H_2O$, is formed. F. Ullik reported **calcium trimolybdate,** $CaO.3MoO_3.6H_2O$, to be formed by boiling an excess of molybdic acid with water having calcium carbonate in suspension, and spontaneously evaporating the clear liquid. The interlaced needles are sparingly soluble in cold water, and easily soluble in hot water. G. Wempe reported what he regarded as hemihydrated normal strontium molybdate, but his analytical data agree better with **strontium trimolybdate,** $SrO.3MoO_3.\frac{1}{2}H_2O$. It was obtained by evaporating a soln. of the octomolybdate to dryness, and washing the product with cold water. The white amorphous mass is sparingly soluble in cold water, but easily soluble in hot water. L. F. Svanberg and H. Struve prepared **barium trimolybdate,** $BaO.3MoO_3.3H_2O$, as a flocculent precipitate by adding barium chloride to a soln. of potassium trimolybdate. The more soluble sodium salt can be used. The salt loses its water when heated; it melts at a red-heat. The hydrate is slightly soluble in water.

F. Ullik obtained **magnesium trimolybdate,** $MgO.3MoO_3.10H_2O$, by spontaneously evaporating a soln. of the normal molybdate in an excess of acetic acid. The acicular crystals are sparingly soluble in cold water, but freely soluble in hot water. F. Ullik obtained a mass of acicular crystals of **zinc trimolybdate,** $ZnO.3MoO_3.10H_2O$, by spontaneously evaporating the filtrate from a soln. obtained by boiling a mol of zinc carbonate with 4 mols of molybdenum trioxide. The salt is sparingly soluble in cold water, and freely soluble in hot water. E. Manassewitsch obtained the trimolybdate by double decomposition of hot or cold soln. of sodium tetramolybdate and a zinc salt. At 120°, the salt loses 4 mols. of water, and the rest at 140°.

F. Ullik prepared **cobaltous trimolybdate,** $CoO.3MoO_3.10H_2O$, by boiling a soln. of an excess of molybdic acid with cobalt carbonate and spontaneously evaporating the filtered liquid. The rose-coloured needles are sparingly soluble in cold water, and freely soluble in hot water. E. Marckwald obtained **sodium cobaltous trimolybdate,** $Na_2O.2CoO.6MoO_3.18H_2O$, by evaporating the mother-liquor obtained in the preparation of the 3 : 3 : 14 : 50-paramolybdate, over sulphuric acid. This salt may be a mixture $Na_2O.2MoO_3+2(CoO.2MoO_3)$.

E. Marckwald prepared **nickelous trimolybdate,** $NiO.3MoO_3.18H_2O$, by evaporating a soln. of eq. proportions of nickelous chloride and sodium paramolybdate. The green crystals are sparingly soluble in cold water, and easily soluble in hot water.

References.

[1] L. F. Svanberg and H. Struve, *Svenska Akad. Handl.*, **1**. 9, 1848 ; *Journ. prakt. Chem.*, (1), **44**. 257, 1848 ; *Phil. Mag.*, (3), **33**. 409, 524, 1848 ; H. Struve, *Bull. Acad. St. Petersburg*, (2), **12**. 142, 1854 ; *Journ. prakt. Chem.*, (1), **61**. 453, 1854 ; A. Rosenheim, *Zeit. anorg. Chem.*, **11**. 225, 1896 ; E. Groschuff, *ib.*, **58**. 113, 1908 ; G. Wempe, *ib.*, **78**. 298, 1912 ; *Beiträge zur Kenntnis der Molybdate*, München, 1911 ; E. Marckwald, *Ueber die Molybdate des Kobalts, Nickels, Mangans, Eisens, Aluminiums und Chroms*, Berlin, 1895 ; G. Canneri, *Gazz. Chim. Ital.*, **60**. 113, 1930 ; F. Mauro, *Gazz. Chim. Ital.*, **18**. 120, 1888 ; *Atti Accad. Lincei*, (4), **4**. 481, 1888 ; A. Scacchi, *ib.*, (4), **4**. 478, 1888 ; F. Ullik, *Sitzber. Akad. Wien*, **55**. 767, 1867 ; **60**. 295, 1869 ; *Liebig's Ann.*, **144**. 204, 1867 ; **153**. 373, 1870 ; A. Atterberg, *Svenska Akad. Handl.*, **12**. 5, 1873 ; *Oefvers. Akad. Stockholm*, **30**. 4, 1873 ; R. D. Hall, *Journ. Amer. Chem. Soc.*, **29**. 690, 1907 ; A. Classen, *Journ. prakt. Chem.*, (1), **93**. 446, 1864 ; F. Parmentier, *Compt. Rend.*, **94**. 1713, 1882 ; A. Péchard, *ib.*, **144**. 1358, 1858 ; M. Brand, *Ueber Molybdate, Sulfomolybdate, und Phosphormolybdate des Lithiums*, Bern, 1905 ; F. Ephraim and M. Brand, *Zeit. anorg. Chem.*, **64**. 258, 1909 ; F. Ephraim and H. Herschfinkel, *ib.*, **64**. 266, 1909 ; H. Herschfinkel, *Ueber Molybdate, Sulfomolybdate, Phosphor-, und Arsenomolybdate des Rubidiums und Cæsiums*, Bern, 1907 ; A. Junius, *Beiträge zur Kenntnis der Molybdate*, Berlin, 1905 ; *Zeit. anorg. Chem.*, **46**. 428, 1905 ; F. Hoermann, *ib.*, **177**. 145, 1928 ; M. Amadori, *Atti Ist. Veneto*, **72**. ii, 893, 1916 ; J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817 ; *Ann. Chim. Phys.*, (2), **17**. 5, 1821 ; *Pogg. Ann.*, **4**. 153, 1825 ; **6**. 331, 369, 1826 ; **7**. 261, 1826.

[2] L. F. Svanberg and H. Struve, *Svenska Akad. Handl.*, **1**. 9, 1848 ; *Journ. prakt. Chem.*, (1), **44**. 257, 1848 ; *Phil. Mag.*, (3), **33**. 409, 524, 1848 ; J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817 ; *Ann. Chim. Phys.*, (2), **17**. 5, 1921 ; *Pogg. Ann.*, **4**. 153, 1825 ; **6**. 331, 369, 1826 ; **7**. 261, 1826 ; F. Mauro, *Gazz. Chim. Ital.*, **11**. 214, 1881 ; A. Laurent, *Ann. Chim. Phys.*, (2), **67**. 219, 1838 ; W. Lotz, *ib.*, (3), **43**. 246, 1855 ; *Journ. prakt. Chem.*, (1), **63**. 209, 1854 ; *Liebig's Ann.*, **91**. 49, 1854 ; F. Ullik, *ib.*, **144**. 204, 320, 1867 ; *Sitzber. Akad. Wien*, **55**. 767, 1867 ; M. Delafontaine, *Journ. prakt. Chem.*, (1), **95**. 136, 1865 ; *Liebig's Ann.*, **127**. 293, 1866 ; *Arch. Sciences Genève*, (2), **23**. 5, 1865 ; J. C. G. de Marignac, *ib.*, (2), **14**. 271, 1858 ; *Compt. Rend.*, **42**. 288, 1856 ; A. Carnot, *ib.*, **109**. 1889 ; E. Darmois and J. Périn, *ib.*, **177**. 762, 1923 ; N. J. Berlin, *Journ. prakt. Chem.*, (1), **49**. 444, 1850 ; R. L. May, *Sitzber. Akad. Wien*, **37**. 25, 1859 ; *Journ. prakt. Chem.*, (1), **78**. 326, 1859 ; F. E. Zenker, *ib.*, (1), **58**. 257, 486, 1853 ; J. G. Gentele, *ib.*, (1), **81**. 411, 1860 ; F. E. Brown and J. E. Snyder, *Journ. Amer. Chem. Soc.*, **47**. 2671, 1925 ; G. vom Rath, *Pogg. Ann.*, **110**. 101, 1860 ; C. F. Rammelsberg, *ib.*, **127**. 298, 1866 ; W. Delffs, *ib.*, **85**. 450, 1852 ; H. Rose, *ib.*, **75**. 319, 1848 ; W. Haidinger, *Edin. Journ. Science*, **1**. 100, 1824 ; H. Flemming, *Jena Zeit.*, **4**. 33, 1868 ; *Bull. Soc. Chim.*, (2), **10**. 235, 1868 ; A. Werncke, *Zeit. anal. Chem.*, **14**. 12, 1875 ; E. Marckwald, *Ueber die Molybdate des Kobalts, Nickels, Mangans, Eisens, Aluminiums, und Chroms*, Berlin, 1895 ; F. Westphal, *Beiträge zur Kenntnis der molybdänsauren Salze*, Berlin, 1895 ; J. Terwelp, *Beiträge zur Elektrochemie der Molybdate*, Berlin, 1903 ; A. Junius, *Beiträge zur Kenntnis der Molybdate*, Berlin, 1905 ; *Zeit. anorg. Chem.*, **46**. 428, 1905 ; G. Wempe, *ib.*, **78**. 298, 1912 ; *Beiträge zur Kenntnis der Molybdate*, München, 1911 ; H. Copaux, *Compt. Rend.*, **156**. 1771, 1913 ; S. Posternak, *ib.*, **170**. 930, 1920 ; **171**. 1058, 1213, 1920 ; **172**. 114, 597, 1921 ; A. Travers and L. Malaprade,

ib., **183**. 292, 533, 1926 ; *Bull. Soc. Chim.*, (4), **39**. 1408, 1543, 1926 ; L. Forsén, *Compt. Rend.*, **172**. 215, 327, 681, 1921 ; A. Lancien, *ib.*, **144**. 1434, 1907 ; *Bull. Soc. Pharm.*, **15**. 132, 1908 ; A. Rosenheim, J. Felix and F. Pinsker, *Zeit. anorg. Chem.*, **79**. 292, 1913 ; J. Felix, *Zur Kenntnis einiger Polymolybdänate und des Molybdänsäuredihydrats*, Berlin, 1912 ; M. Pieck, *Ueber Heteropolyaquosäuren*, Berlin, 1916 ; M. Brand, *Ueber Molybdate, Sulfomolybdate und Phosphormolybdate des Lithiums*, Bern, 1905 ; F. Ephraim and M. Brand, *Zeit. anorg. Chem.*, **64**. 258, 1909 ; B. Glassmann, *Ber.*, **38**. 193, 1905 ; S. E. Moody, *Amer. Journ. Science*, (4), **25**. 76, 1908 ; S. Dushman, *Journ. Phys. Chem.*, **8**. 453, 1904 ; W. Muthmann and W. Nagel, *Ber.*, **31**. 1836, 1898 ; F. Ephraim and H. Herschfinkel, *Zeit. anorg. Chem.*, **64**. 266, 1909 ; H. Herschfinkel, *Ueber Molybdate, Sulfomolybdate, Phosphor- und Arsenomolybdate des Rubidiums und des Cæsiums*, Bern, 1907 ; E. Manassewitsch, *Beiträge zur Kenntnis der Molybdate des Zinks und Cadmiums*, Bern., 1900 ; G. A. Barbieri, *Atti Accad. Lincei*, (5), **17**. i, 540, 1908 ; (5), **20**. i, 18, 1911 ; (5), **23**. 334, 805, 1914 ; E. Billows, *Zeit. Kryst.*, **50**. 550, 1912 ; H. Steinmetz, *ib.*, **56**. 157, 1921 ; A. Cleve, *Oefvers, Akad. Förh.*, **58**. 573, 1902 ; *Zeit. anorg. Chem.*, **32**. 129, 1902 ; J. N. Rakshit, *Zeit. Elektrochem.*, **31**. 97, 1925 ; A. Lottermoser, *Zeit. Koll.*, **30**. 346, 1922 ; A. Rosenheim, *Zeit. anorg. Chem.*, **15**. 180, 1897 ; **93**. 273, 1915 ; **96**. 139, 1916 ; J. Sand and F. Eisenlohr, *ib.*, **52**. 68, 87, 1907 ; E. Groschuff, *ib.*, **58**. 113, 1908 ; L. Ott, *Elektrolyse geschmolzener Molybdate und Vanadate*, München, 1911 ; J. Sand, *Ber.*, **39**. 2038, 1906 ; P. Klason, *ib.*, **34**. 153, 1901.

[3] N. J. Berlin, *Journ. prakt. Chem.*, (1), **49**. 444, 1850 ; L. Kämmerer, *ib.*, (2), **6**. 358, 1873 ; P. Klason, *Ber.*, **34**. 153, 1901 ; W. Muthmann and W. Nagel, *ib.*, **31**. 1836, 1898 ; F. Westphal, *Beiträge zur Kenntnis der molybdänsauren Salze*, Berlin, 1895 ; F. Ephraim and M. Brand, *Zeit. anorg. Chem.*, **64**. 258, 1909 ; M. Brand, *Ueber Molybdate, Sulfomolybdate, und Phosphormolybdate des Lithiums*, Bern, 1905 ; G. Wempe, *Beiträge zur Kenntnis der Molybdate*, München, 1911 ; *Zeit. anorg. Chem.*, **78**. 298, 1912 ; A. Junius, *ib.*, **46**. 428, 1905 ; *Beiträge zur Kenntnis der Molybdate*, Berlin, 1905 ; H. Struve, *Bull. Acad. St. Petersburg*, (2), **12**. 145, 1853 ; *Journ. prakt. Chem.*, (1), **61**. 453, 1854 ; L. F. Svanberg and H. Struve, *Svenska Akad. Handl.*, **1**. 9, 1848 ; *Journ. prakt. Chem.*, (1), **44**. 257, 1848 ; *Phil. Mag.*, (3), **33**. 409, 524, 1848 ; F. Ullik, *Sitzber. Akad. Wien*, **55**. 767, 1867 ; **60**. 295, 1869 ; *Liebig's Ann.*, **144**. 204, 320, 1867 ; **153**. 373, 1870 ; E. Groschuff, *Zeit. anorg. Chem.*, **58**. 113, 1908 ; A. Rosenheim, *ib.*, **96**. 139, 1916 ; F. Hoermann, *ib.*. **177**. 145, 1928 ; F. Ephraim and H. Herschfinkel, *ib.*, **64**. 266, 1909 ; H. Herschfinkel, *Ueber Molybdate, Sulfomolybdate, Phosphor- und Arsenomolybdate des Rubidiums und des Cæsiums*, Bern., 1907 ; M. Delafontaine, *Arch. Sciences Genève*, (2), **23**. 9. 1865 ; (2), **30**. 235, 1867 ; E. Manassewitsch, *Beiträge zur Kenntnis der Molybdate des Zinks und Cadmiums*, Bern, 1900 ; E. Marckwald, *Ueber die Molybdate des Kobalts, Nickels, Mangans, Eisens, Aluminiums, und Chroms*, Berlin, 1895 ; M. Amadori, *Atti Ist. Veneto*, **72**. ii, 893, 1916 ; G. Jander and A. Winkle, *Zeit. phys. Chem.*, **149**. 97, 1930 ; G. Jander, *Metallbörse*, **20**. 1855, 1930.

§ 13. The Tetra-, Penta-, Hexa- and Hepta-Molybdates

According to A. Rosenheim and J. Felix,[1] the salt represented by N. J. Berlin as **ammonium tetramolybdate,** $(NH_4)_2O.4MoO_3.2H_2O$, is probably the trimolybdate. There is also some uncertainty about the tetramolybdate reported by F. Westphal, A. Rosenheim, and D. Asch to be formed by heating the paramolybdate for some days at 140° to 150° ; and that obtained by F. Westphal by boiling a soln. of paramolybdate, or by heating the paramolybdate in a sealed tube at 150° to 200°. This product was anhydrous, and water is an essential constituent of the tetramolybdate which A. Rosenheim and J. Felix represent by the formula $(NH_4)_6H_4[H_2(Mo_2O_7)_6].3H_2O$. P. Klason gave $3NH_3.6MoO_3.5H_2O$ for the formula of the salt, but his analysis agrees better with $(NH_4)_2Mo_4O_{13}.2\frac{1}{2}H_2O$. P. Klason prepared this salt by treating a cold soln. of ammonium paramolybdate with the calculated quantity of hydrochloric acid, crystallization begins in about 12 hrs. G. Wempe, and F. Westphal used a similar process with warm soln. ; and A. Junius electrolyzed a soln. of 60 grms. of ammonium paramolybdate in 350 c.c. of water, by a current of 4 amp. for 40 min. in a compartment cell. In all these cases, the soln. furnish crystals of $(NH_4)_2Mo_4O_{13}.2\frac{1}{2}H_2O$. A. Travers and L. Malaprade showed that the tetramolybdates are obtained by neutralizing the acid under conditions which limit the reversal of the reaction by hydrolysis—*vide supra*, molybdic acid. G. Wempe supposed that the crystals are triclinic ; and 100 grms. of a sat. soln., at 15°, 18°, and 32°, contained, respectively, 3·5200, 3·6711, and 4·5961 grms. of the hydrated salt ; and had the sp. gr. 1·03, 1·04, and 1·05, respectively. P. Klason said that the soln. in water over 35° is partially decomposed into trimolybdate. G. Wempe gave for the conductivity, λ, of an eq. of the salt in 10, 20, and 40 litres of water respectively, λ=73·2, 98·8, and 120·4. The aq. soln. reddens methyl-orange, and litmus; acids give no precipitate; barium chloride, a white precipitate; magnesia mixture, a white precipitate; stannous chloride, a green precipitate; ferrous sulphate, a bluish-white precipitate; potassium ferrocyanide, a reddish-brown coloration; and silver nitrate, a white, curdy precipitate. G. Canneri obtained a series of complex salts typified by **ammonium tetrahydroxylaminotetramolybdate,** $(NH_4)_2O.4NH_2OH.4MoO_3$; **sodium tetrahydroxylaminotetramolybdate,** $Na_2O.4NH_2OH.4MoO_3$; **potassium tetrahydroxylaminotetramolybdate,** $K_2O.4NH_2OH.4MoO_3$; and **methylamine tetrahydroxylaminotetramolybdate,** $(CH_6N_3)_2O.4NH_2OH.4MoO_3$—*vide supra.*

F. Ephraim and M. Brand obtained amorphous **lithium tetramolybdate,** $Li_2Mo_4O_{13}.7H_2O$, by F. Ullik's method for the sodium salt; but G. Wempe could not prepare this salt. F. Hoermann, Fig. 13, found that the salt has an incongruent m.p. at 568°. F. Ullik prepared **sodium tetramolybdate,** $Na_2O.4MoO_3.5\frac{1}{2}H_2O$, by putting drops of a hot, conc. soln. of the trimolybdate on a glass plate, and allowing it to evaporate spontaneously. The *hemihenahydrate* appears as a transparent gum-like mass which can be kept unchanged in a closed vessel; but in air, it becomes opaque and passes into the trimolybdate. It retains 2 mols. of water at 100°, and melts to a yellow liquid at a red-heat; the liquid forms a crystalline mass when cold. At a higher temp. molybdenum trioxide volatilizes. The salt is freely soluble in cold water, and when the aq. soln. is spontaneously evaporated, it deposits the trimolybdate. It is open to question whether this product is really a chemical individual. F. Hoermann found that the salt has an incongruent m.p. at 515°—Fig. 14. S. J. Diatschkovsky and A. V. Dumansky obtained a complex $Na_2O(MoO_3)_4$ and found its conductivity and f.p. depressions corresponded with those obtained by the gradual addition of hydrochloric acid to soln. of sodium molybdate—*vide supra,* colloidal molybdic acid. F. Ullik, however, obtained a crystalline *hexahydrate* which A. Rosenheim and J. Felix represented by $Na_2Mo_4O_{13}.6H_2O$, or $Na_6H_4[H_2(Mo_2O_7)_6.].21H_2O$. F. Ullik, and G. Wempe obtained it by treating a conc. soln. of normal sodium molybdate with the theoretical quantity of hydrochloric acid; the precipitate first formed redissolves, and the liquid soon begins to deposit crystals of the tetramolybdate. F. Ullik obtained this salt by adding one or two mols of sodium carbonate to a mol of the octomolybdate—A. Rosenheim and J. Felix used 2 mols of sodium hydroxide. G. Wempe obtained the salt by double decomposition with sodium sulphate and ammonium tetramolybdate. A. Rosenheim and J. Felix said that the salt is an *octomolybdate.* F. Ullik found that the hexahydrate consists of microscopic crystals, which dissolve slowly in cold water and quickly in hot water forming a pale yellow soln. G. Wempe said that the salt consists of masses of needle-like crystals, and that, when saturated, 100 c.c. of soln. at 21° contain 28·39 grms. of the hexahydrate, of sp. gr. 1·47. A. Rosenheim and J. Felix gave for the conductivity, λ, of an eq. of $Na_2Mo_4O_{13}$.aq. in v litres of water at 25°,

v . . .	32	64	128	256	512	1024
λ . . .	98·8	108·3	120·3	130·4	145·0	162·8 mhos.

L. F. Svanberg and H. Struve obtained **potassium tetramolybdate,** $K_2O.4MoO_3.nH_2O$, from the liquid obtained by adding nitric acid to a soln. of molybdic acid in potassium carbonate. A. Rosenheim showed that it is a heptahydrate, $K_2O.4MoO_3.7H_2O$, or, as he represented it, $K_6H_4[H_2(Mo_2O_7)_6].18H_2O$; and he found that a cold soln. of a mol of potassium carbonate and 4 mols of molybdic acid passes quickly into one of the trimolybdate, particularly when warm; and G. Wempe always obtained trimolybdate from a soln. of molybdic acid and sodium carbonate treated with the quantity of hydrochloric acid theoretically required to form the tetramolybdate. M. Amadori's thermal analysis shows that the tetramolybdate can exist. A. Rosenheim and J. Felix obtained crystals of the salt by warming for a few minutes a soln. of sodium octomolybdate and potassium chloride. The microcrystalline powder of the heptahydrate retains a mol. of water at 100°. It is sparingly soluble in cold water, and is decomposed by boiling water with the separation of trimolybdate.

G. Wempe prepared **rubidium tetramolybdate,** $Rb_2O.4MoO_3.4H_2O$, by filtering a hot soln. of rubidium carbonate and an excess of molybdic acid, and rapidly evaporating the liquid. The *tetrahydrate* is an amorphous, white powder which is readily soluble in cold water. G. Wempe also obtained crystals of the anhydrous salt by evaporating on the water-bath a soln. of rubidium paramolybdate treated with the calculated amount of hydrochloric acid. If the crystalline scales are really anhydrous, the formula does not fit A. Rosenheim's theory of the constitution of these salts. F. Ephraim and H. Herschfinkel, however, found that the salt is a *hemihydrate*, $Rb_2Mo_4O_{13}.\frac{1}{2}H_2O$, if obtained from boiling soln.; and the mother-liquor deposits crystals of the paramolybdate, but if it be treated with nitric acid of sp. gr. 1·20, added drop by drop, the *hemipentahydrate* is formed. W. Muthmann and W. Nagel obtained **cæsium tetramolybdate,** $Cs_2O.4MoO_4$, by melting a mol of cæsium carbonate with 3 mols of molybdenum trioxide, and boiling the cold mass repeatedly with water; evaporation over sulphuric acid of the hot extract furnishes quadratic plates of the *dihydrate*, $Cs_2O.4MoO_3.2H_2O$. G. Wempe obtained a *trihydrate*, $Cs_2O.4MoO_3.3H_2O$, by evaporating rapidly on a glass plate drops of a hot filtered soln. of cæsium carbonate and an excess of molybdic acid.

G. Wempe prepared **silver tetramolybdate,** $Ag_2O.4MoO_3.6H_2O$, by treating a hot soln. of ammonium tetramolybdate with an excess of a hot soln. of silver sulphate. The white, flocculent precipitate is coloured green when heated, and it melts to a liquid which, on cooling, forms a yellow crystalline mass. It is decomposed by hot water, with the separation of molybdenum trioxide.

F. Ullik prepared **calcium tetramolybdate,** $CaMo_4O_{13}.9H_2O$, by the action of molybdic acid on calcium carbonate suspended in water. The crystalline salt has not been obtained, otherwise the calcium and sodium salts have analogous properties. F. Ullik obtained **barium tetramolybdate,** $BaMo_4O_{13}.5H_2O$, by the action of hot water on the octohydrate; and A. Rosenheim and J. Felix, by the action of barium chloride on a soln. of sodium octomolybdate, and warming the clear soln. The microcrystalline precipitate loses four-fifths of its water at 120° in agreement with the formula $Ba_3H_4[H_2(Mo_2O_7)_6].12H_2O$. G. Wempe obtained $BaMo_4O_{13}.3{\cdot}5H_2O$, as an amorphous precipitate by the action of barium chloride on a soln. of sodium tetramolybdate. A. Travers and L. Malaprade obtained $BaO.4MoO_3.9H_2O$, from soln. of barium metatungstate and tetramolybdic acid at 70°. G. Wempe could not prepare **magnesium tetramolybdate** by the action of magnesium carbonate on an excess of a boiling soln. of molybdic acid—the product appeared to be the normal molybdate. F. Ullik reported that **zinc tetramolybdate,** $ZnMo_4O_{13}.8H_2O$, is formed as in the case of the calcium salt.

G. Canneri obtained **ammonium dimolybditotetramolybdate,** $2(NH_4)_2O.Mo_2O_5.4MoO_3.8H_2O$; as well as **sodium dimolybditotetramolybdate,** $Na_2O.Mo_2O_5.4MoO_3.10H_2O$; and **potassium dimolybditomolybdate,** $2K_2O.Mo_2O_5.4MoO_3.5H_2O$. By reducing alkali dimolybdates (*q.v.*), he also prepared **lithium hypomolybditotetramolybdate,** $Li_2O.4MoO_3.MoO_2$; **sodium hypomolybditotetramolybdate,** $Na_2O.4MoO_3.MoO_2$; **sodium hypomolybditopentamolybdate,** $Na_2O.5MoO_3.MoO_2$; and **potassium hypomolybditopentamolybdate,** $K_2O.5MoO_3.MoO_2$. By the action of hydrogen chloride near 600°, compounds of the type $O:Mo[O.MoO_2.O.MoO_2.O.R.]_2$, where R denotes Na or Li; and $O:Mo(OR)[O.(MoO_2.O)_5.R]$, where R denotes Na or K, were obtained.

F. Jean [2] reported **ammonium pentamolybdate,** $2(NH_4)_2O.5MoO_3.H_2O$, to separate as an amorphous precipitate when a boiling soln. of ammonium molybdate is treated with ammonium chloride. This result has not been confirmed, and a similar remark applies to L. F. Svanberg and H. Struve's report of the formation of **potassium pentamolybdate** by the action of nitric acid on a soln. of molybdic acid in one of potassium carbonate.

L. F. Svanberg and H. Struve reported **silver pentamolybdate,** $2Ag_2O.5MoO_3$, to be formed by treating a soln. of potassium trimolybdate with silver nitrate. The mass had a variable composition, and was somewhat soluble in water. A. Junius could not prepare it; and it is doubtful if it is a chemical individual. E. Dittler obtained **lead pentamolybdate,** $2PbO.5MoO_3$, by adding a hot, conc. soln. of lead chloride to a hot, 6 per cent. soln. of ammonium 5 : 12-molybdate so long as an additional drop produced no turbidity. The yellowish-green, amorphous product forms bluish-green, hexagonal or trigonal prisms at 115°. They are optically negative, insoluble in water; soluble in nitric acid; soluble in hydrochloric acid (1 : 80); and soluble in a soln. of sodium carbonate, and the soln. on standing deposits basic lead carbonate, $Pb_3(OH)_2(CO_3)_2$.

E. Marckwald obtained **ammonium cobaltous pentamolybdate,** $9\{2(NH_4)_2O.5MoO_3\}$-$5\{2CoO.5MoO_3\}.118H_2O$, as a red crystalline mass, by evaporating the filtrate after boiling a mixed soln. of eq. proportions of cobaltous chloride and ammonium paramolybdate; he also obtained red crystals of $4(NH_4)_2O.2CoO_3.15MoO_3.20H_2O$.

For some hexamolybdates, *vide infra*, dodecamolybdates. The **ammonium hexamolybdate,** $3NH_3.6MoO_3.5H_2O$, of P. Klason[3] was shown previously to be more probably a tetramolybdate. P. Klason also reported that a sample of commercial molybdic acid was best represented by $NH_3.3MoO_3.\frac{1}{2}H_2O$, and it is obtained by evaporating a mixture of ammonium paramolybdate with an excess of nitric acid. This product—if the statements are correct—can be regarded as anhydrous ammonium hexamolybdate, $(NH_4)_2O.6MoO_3$. P. Klason also reported what he regarded as *ammonium pentahydrotrimolybdate*, $(NH_4)H_5Mo_3O_{12}$, or $NH_3.3MoO_3.3H_2O$, but may be also regarded as a *pentahydrate*, $(NH_4)_2O.6MoO_3.5H_2O$. It was obtained by adding the calculated quantity of N-HCl to a cold soln. of ammonium paramolybdate, and crystallizing. The needle-like crystals lose 2 mols. of water over phosphorus pentoxide at ordinary temp. They are sparingly soluble in cold water, and more soluble in hot water—but with partial decomposition. A. Rosenheim regarded the hexamolybdates as hexahydrododecamolybdates, *e.g.* $(NH_4)_4H_6[H_2(Mo_2O_7)_6].nH_2O$. G. Jander and A. Winkel found the alkali hexamolybdate, $R_5[HMo_6O_{21}]$, to be stable in the range $[H^{\cdot}]=10^{-4\cdot5}$ to $10^{-1\cdot6}$; and gave for the diffusion coeff. of the anion, 0·28. G. Jander described the conditions of stability of the acid. According to E. Marckwald, a soln. of sodium di- or para-molybdate and nickelous chloride gives prismatic crystals of **sodium nickelous hexamolybdate,** $Na_2O.2NiO.6MoO_3$, in prismatic crystals which dissolve without decomposition in cold water, but are decomposed by hot water.

S. Posternak prepared **ammonium hydroheptamolybdate,** $(NH_4O)_3MoO(O.MoO_2)_5O.MoO_2(OH)$, from a boiling soln. of ammonium molybdate with molybdic oxide; and **ammonium trihydroheptamolybdate,** $(NH_4O)(HO)_2MoO(O.MoO_2)_5O.MoO_2.OH.H_2O$, as a crystalline crust by warming a soln. of ordinary ammonium molybdate on a water-bath. He supposed the anhydrous paramolybdate (*q.v.*) to be $(NH_4O)_3Mo(O.MoO_2)_5O.MoO(ONH_4)_3$. A. Travers and L. Malaprade discussed the constitution of the salts of $H_6[7MoO_3.3O]$.

References.

[1] N. J. Berlin, *Journ. prakt. Chem.*, (1), **49**. 444, 1850; A. Rosenheim, *Zeit. anorg. Chem.*, **15**. 180, 1897; A. Rosenheim and J. Felix, *ib.*, **79**. 292, 1913; J. Felix, *Zur Kenntnis einiger Polymolybdänate und des Molybdänsauredihydrats*, Berlin, 1912; D. Asch, *Zur Kenntnis der Schwefligmolybdate*, Berlin, 1902; P. Klason, *Ber.*, **34**. 153, 1901; W. Muthmann and W. Nagel, *ib.*, **31**. 1836, 1898; F. Westphal, *Beiträge zur Kenntnis der molybdänsauren Salze*, Berlin, 1895; G. Wempe, *Beiträge zur Kenntnis der Molybdate*, München, 1911; *Zeit. anorg. Chem.*, **78**. 298, 1912; F. Hoermann, *ib.*, **177**. 145, 1928; F. Ephraim and M. Brand, *ib.*, **64**. 258, 1909; M. Brand, *Ueber Molybdate, Sulfomolybdate und Phosphormolybdate des Lithiums*, Bern, 1905; F. Ullik, *Sitzber. Akad. Wien*, **55**. 767, 1867; **60**. 295, 1869; *Liebig's Ann.*, **144**. 2 (4), 320, 1867; **153**. 373, 1870; H. Herschfinkel, *Ueber Molybdate, Sulfomolybdate, Phosphor- und Arsenomolybdate des Rubidiums und Cæsiums*, Bern, 1907; F. Ephraim and H. Herschfinkel, *Zeit. anorg. Chem.*, **64**. 266, 1909; A. Travers and L. Malaprade, *Compt. Rend.*, **183**. 292, 533, 1926; *Bull. Soc. Chim.*, (4), **39**. 1543, 1926; M. Amadori, *Atti Ist. Veneto*, **72**. ii, 893, 1916; S. J. Diatschkovsky and A. V. Dumansky, *Journ. Russ. Phys. Chem. Soc.*, **58**. 630, 1926; G. Canneri, *Gazz. Chim. Ital.*, **57**. 872, 1927; **60**. 113, 1930; L. F. Svanberg and H. Struve, *Svenska Akad. Handl.*, **1**. 9, 1848; *Journ. Prakt. Chem.*, (1), **44**. 257, 1848; *Phil. Mag.*, (3), **33**. 409, 524, 1848.

[2] F. Jean, *Compt. Rend.*, **78**. 1436, 1874; L. F. Svanberg and H. Struve, *Svenska Akad.*

Handl., **1**. 9, 1848 ; *Journ. prakt. Chem.*, (1), **44**. 257, 1848 ; *Phil. Mag.*, (3), **33**. 409, 524, 1848 ; A. Junius, *Beiträge zur Kenntnis der Molybdate*, Berlin, 1905 ; *Zeit. anorg. Chem.*, **46**. 428, 1905 ; E. Dittler, *Zeit. Kryst.*, **53**. 167, 1914 ; E. Marckwald, *Ueber die Molybdate des Kobalts, Nickels, Mangans, Eisens, Aluminiums, und Chroms*, Berlin, 1895.

[3] P. Klason, *Ber.*, **34**. 153, 1901 ; A. Rosenheim, *Zeit. anorg. Chem.*, **96**. 139, 1916 ; E. Marckwald, *Ueber die Molybdate des Kobalts, Nickels, Mangans, Eisens, Aluminiums, und Chroms*, Berlin, 1895 ; S. Poternak, *Compt. Rend.*, **171**. 1058, 1920 ; A. Travers and L. Malaprade, *ib.*, **183**. 292, 533, 1926 ; G. Jander and A. Winkel, *Zeit. phys. Chem.*, **149**. 97, 1930 ; G. Jander, *Metallbörse*, **20**. 1855, 1930.

§ 14. The Octo-, Ennea-, and Deca-Molybdates

F. Mylius [1] added the theoretical quantity of hydrochloric, sulphuric, or nitric acid to a soln. of ammonium paramolybdate, and obtained colourless needles which he represented by the formula $NH_3.4MoO_3.6H_2O$, or $(NH_4)_2O.8MoO_3.11H_2O$, but which A. Rosenheim regarded as **ammonium octomolybdate,** $(NH_4)_2O.8MoO_3.13H_2O$, and A. Rosenheim and J. Felix, as *ammonium heptahydrododecamolybdate*, $(NH_4)_3H_7[H_2(MoO_7)_6].20H_2O$. A. Rosenheim obtained his salt by the action of sulphur dioxide on ammonium tetramolybdate suspended in water, and crystallizing the soln. over sulphuric acid. As indicated by the formulæ there are differences of opinion as to the water-content. F. Mylius said that when the salt is warmed the expulsion of the water is attended by the loss of some ammonia, and when all the ammonia is driven off, the product is green owing to some reduction. The salt is sparingly soluble in cold water, and rather more soluble in hot water, and at about 60°, a salt containing less water slowly separates. A. Rosenheim suggested that this is the *heptahydrate* reported by P. Klason to be formed by treating a warm soln. of the decamolybdate with ammonium chloride, and which P. Klason regarded as $3NH_3.12MoO_3.12H_2O$. F. Mylius added that the aq. soln. of ammonium octomolybdate has an acidic reaction ; it liberates carbon dioxide from carbonates ; it coagulates albumen ; and, unlike normal molybdates, it gives no precipitate with nitric acid—the soln., however, gradually deposits a salt with less ammonia, or a hydrated molybdenum trioxide.

G. Wempe obtained **lithium octomolybdate,** $Li_2O.8MoO_3.11H_2O$, from a conc. soln. of ammonium tetramolybdate and an excess of lithium sulphate. The transparent needles are soluble in water, and when strongly heated, lose some molybdenum oxide. F. Ephraim and M. Brand could not make this salt. F. Ullik prepared **sodium octomolybdate,** $Na_2O.8MoO_3.17H_2O$, by mixing a soln. of normal sodium molybdate with the calculated quantity of hydrochloric acid, and spontaneously evaporating the clear liquid. A. Rosenheim and J. Felix, and G. Wempe employed a similar mode of preparation. A. Rosenheim and J. Felix also obtained it from a soln. of the normal molybdate sat. with molybdic acid ; and they represented it by the formula $Na_3H_7[H_2(Mo_2O_7)_6].21H_2O$. S. J. Diatschkovsky and A. V. Dumansky prepared the complex $Na_2O(MoO_3)_8$ and found that its conductivity and f.p. depression corresponded with those obtained by adding hydrochloric acid gradually to a soln. of sodium molybdate when colloidal particles appear—*vide supra*, colloidal molybdic acid. According to V. von Zepharovich, the *heptadecahydrate* crystallizes in monoclinic crystals with the axial ratios $a:b:c=1{\cdot}975:1:$—, and $\beta=96°\ 1'$. The crystals are stable at 0°, but at room temp., in air, they lose water and decompose. The loss of water is completed at 160°–180°. The heptadecahydrate is readily soluble in cold or hot water, and crystallizes unchanged when the aq. soln. is evaporated spontaneously ; but if the crystals have lost water by efflorescence, the salt becomes sparingly soluble, and if washed with water, sodium decamolybdate remains. A. Rosenheim and J. Felix found the conductivity, λ mhos, of an eq. of the salt in v litres of water at 25° to be :

v .	16	32	64	128	256	512	1024
λ .	144·8	196·9	303·6	349·3	377·9	406·4	410·6

The large increase in the conductivity indicates that an acid salt rapidly forms hydrogen ions with increasing dilution. The change in the sp. conductivity, *K*, of 25 c.c. of $\frac{1}{32}N$-$Na_2Mo_2O_{25}$ at 25°, when $\frac{1}{102}N$-NaOH is gradually added to 25 c.c. of $\frac{1}{32}N$-$Na_2Mo_8O_{25}$, is as follows, where NaOH represents the number of mols of sodium hydroxide added per mol of $Na_2Mo_8O_{25}$:

NaOH .	0	0·378	1·260	1·764	2·015	2·267	3·023	3·525
K . .	0·04708	0·04418	0·03411	0·02967	0·03018	0·03030	0·03332	0·03550

This means that with the addition of alkali, the acid is neutralized and the conductivity decreases, and when about 2 mols of alkali per mol of salt have been added, sodium tetramolybdate is formed, and the conductivity increases, owing to the increasing alkalinity of the soln. Aq. soln. of the octomolybdate are as unstable as the solid salt, and at their b.p. the liquid becomes turbid owing to the separation of decamolybdate. *Vide infra*, the hexadecamolybdates, for a polymerized form.

F. Ullik prepared **potassium octomolybdate,** $K_2O.8MoO_3.13H_2O$, by dissolving potassium trimolybdate in a soln. of molybdic acid ; the precipitate dissolves when the liquid is warmed, and when the filtered soln. is cooled, the salt separates out in crystals. A. Rosenheim, A. Rosenheim and J. Felix, and D. Asch obtained it by passing sulphur dioxide into an aq. soln. of the tetramolybdate, and crystallizing the liquid over sulphuric acid ; and G. Wempe, by the action of potassium sulphate on a hot soln. of ammonium tetramolybdate. It is not formed when potassium molybdate is treated with the calculated quantity of hydrochloric acid, because the trimolybdate is formed instead. According to F. Ullik, the prismatic crystals are decomposed by water forming a sparingly-soluble powder ; when the salt is heated, water is given off, and at a red-heat, the product fuses. G. Wempe said that the salt forms monoclinic needles, which easily dissolve in warm water. These properties as well as the mode of preparation made A. Rosenheim doubt if G. Wempe's salt is really the octomolybdate. A. Rosenheim and J. Felix regarded it as *potassium heptahydrododecamolybdate,* $K_3H_7[H_2(Mo_2O_7)_6].15H_2O$. G. Wempe reported **rubidium octomolybdate,** $Rb_2O.8MoO_3.4H_2O$, to be formed as in the case of the potassium salt ; and the needle-like crystals are said to be probably monoclinic. They effloresce in air ; and are sparingly soluble in cold water, and readily soluble in hot water. The corresponding **cæsium octomolybdate** has not been prepared.

According to F. Ullik, **calcium octomolybdate,** $CaMo_8O_{25}.18H_2O$—A. Rosenheim and J. Felix gave $(\frac{1}{2}Ca)_3H_7[H_2(Mo_2O_7)_6].22H_2O$—is formed by the action of the calculated quantity of hydrochloric acid on normal calcium molybdate, and allowing the liquid to evaporate spontaneously. A. Rosenheim and J. Felix obtained it in a similar manner. The small, prismatic crystals are very similar to those of the other octomolybdates. The salt gives off water when heated, and the residue begins to fuse at a red-heat. The salt is almost insoluble in cold water, but in hot water it is soluble. G. Wempe represented the amorphous salt obtained by mixing soln. of eq. quantities of sodium tetramolybdate and calcium chloride, by the formula $CaMo_8O_{25}.17H_2O$. He also obtained what he regarded as **strontium octomolybdate,** $SrMo_8O_{25}.7H_2O$—although his data agree better with $SrMo_{10}O_{31}.12H_2O$—by the action of strontium chloride soln. on one of ammonium tetramolybdate. The acicular crystals are monoclinic or triclinic. F. Ullik prepared **barium octomolybdate,** $BaMo_8O_{25}.18H_2O$—A. Rosenheim and J. Felix gave the formula $(\frac{1}{2}Ba)_3H_7[H_2(Mo_2O_7)_6].22H_2O$—by the action of a warm soln. of molybdic acid on barium carbonate ; by the action of a mol of barium chloride on a soln. of a mol of sodium octomolybdate ; and by pouring a soln. of barium chloride into an aq. soln. of molybdic acid. The filtered soln. is evaporated for crystallization. A. Rosenheim and J. Felix obtained it by the action of 1·75 mols of hydrochloric acid on a mol of normal barium molybdate suspended in water ; the soln. crystallized at ordinary temp. The prismatic crystals decompose with the loss of water when heated, and the residue melts at a dull red-heat. The salt is sparingly soluble in cold water, and is decomposed into the tetramolybdate by hot water. G. Wempe obtained an amorphous powder as a precipitate on treating ammonium tetramolybdate with barium chloride; he represented it by the formula $BaMo_8O_{25}.15H_2O$, and said that it is soluble in cold or hot water. G. Wempe's idea of this compound does not agree with the observations of F. Ullik.

F. Ullik prepared **magnesium octomolybdate,** $MgMo_8O_{25}.20H_2O$, as in the case of the sodium salt, by mixing a mol of normal magnesium molybdate with 1·75 mols of hydrochloric acid. G. Wempe obtained it by the action of magnesium sulphate on a soln. of a molybdate, and represented it by the formula $MgMo_8O_{25}.21H_2O$. V. von Zepharovich said that the prismatic crystals are probably triclinic. The salt effloresces in air; it is dehydrated by heat; it melts at a red-heat; dissolves in cold water, and resembles the other octomolybdates in general properties. G. Wempe also reported **zinc octomolybdate,** $ZnMo_8O_{25}.15H_2O$, to be formed as in the analogous case of magnesium octomolybdate; and similarly also with **cadmium octomolybdate,** $CdMo_8O_{25}.7H_2O$.

A. Lancien obtained anhydrous **uranyl octomolybdate,** $UO_3.8MoO_3$, by the action of sunlight on the paramolybdate (*q.v.*); and the *tridecahydrate,* $UO_3.8MoO_3.13H_2O$, is obtained as prismatic needles when ammonium paramolybdate is precipitated by uranium nitrate and the product treated with excess of acetic acid; the substance obtained is extremely sensitive to light. He measured the rate of change of this substance when exposed to light of various wave-lengths.

A. Meinhard obtained well-defined salts of quadrivalent manganese by the action of potassium fluopermanganite on a paramolybdate. Thus, there were produced **potassium permanganous octomolybdate,** $3K_2O.MnO_2.8MoO_3.7H_2O$, and **ammonium permanganous octomolybdate,** $3(NH_4)_2O.MnO_2.8MoO_3.7\frac{1}{2}H_2O$.

L. F. Svanberg and H. Struve [2] treated barium molybdate with dil. nitric acid and obtained from the liquid six-sided prisms of **barium enneamolybdate,** $BaO.9MoO_3.4H_2O$. The salt is insoluble in cold or hot water, or in water acidulated with nitric acid; and it is incompletely decomposed by sulphuric acid, or by a mixture of sulphuric acid with nitric or hydrochloric acid. R. D. Hall reported **potassium percobaltic enneamolybdate,** $3K_2O.CoO_2.9MoO_3.6\frac{1}{2}H_2O$, to be obtained by boiling a soln. of cobaltous sulphate and potassium paramolybdate with potassium persulphate. E. Marckwald prepared **ammonium nickelous enneamolybdate,** $(NH_4)_2O.3NiO.9MoO_3.25H_2O$, from the mother-liquor of the 6 : 3 : 16 : 29 salt. R. D. Hall reported **potassium pernickelic enneamolybdate,** $3K_2O.NiO_2.9MoO_3.6\frac{1}{2}H_2O$, to be formed by boiling a mixed soln. of potassium paramolybdate and nickelous sulphate with potassium persulphate. A boiling soln. of ammonium molybdate, nickelous sulphate and potassium persulphate furnishes dark purple crystals of **ammonium pernickelic enneamolybdate;** and by adding barium chloride to a soln. of this salt, **barium pernickelic enneamolybdate,** $3BaO.NiO_2.9MoO_3.12H_2O$, is formed.

P. Klason [3] prepared **ammonium decamolybdate,** which he represented by the formula $3NH_3.12MoO_3.12H_2O+MoO_3.8H_2O$, but which can be better represented by $(NH_4)_2O.10MoO_3.13H_2O$. He obtained this salt from a soln. of ammonium paramolybdate mixed with the calculated quantity of *N*-HCl. A. Rosenheim and J. Felix with the same mode of preparation obtained the *enneadecahydrate.* The white powder consists of microscopic prisms which dissolve freely in hot water. The salt can be crystallized unchanged from its aq. soln. evaporated at ordinary temp. If a large porportion of the salt is warmed with a little water, it gradually forms the *trihydrate.* The trihydrate is also produced when a soln. of the normal salt is heated with the necessary amount of hydrochloric acid in a closed vessel at 40°, and likewise by dehydration of the enneadecahydrate over phosphorus pentoxide. The six-sided prisms of the trihydrate are sparingly soluble in water. The solid phase of the enneadecahydrate in contact with water for 20 hrs. is all trihydrate. The solubility of the trihydrate at 25° is 0·33 per cent., and at 100° is 0·447 per cent. of $(NH_4)_2Mo_{10}O_{31}$. The low proportion of water of crystallization found by P. Klason shows that his salt had been partially transformed into the trihydrate.

The transformation of the enneadecahydrate is shown by its decreasing solubility, *S*, per cent. $(NH_4)_2Mo_{10}O_{31}$, when the aq. soln. is kept at 25°.

Time . .	6	16	20	30	40 hrs.
S . .	6·01	2·30	0·33	0·33	0·38 per cent.

F. Ullik obtained **sodium decamolybdate,** $Na_2O.10MoO_3.21(\text{or } 22)H_2O$, from a soln. of sodium trimolybdate or carbonate in the calculated quantity of molybdic acid; and A. Rosenheim and J. Felix, by treating an ice-cold, conc. soln. of normal sodium molybdate with more than the calculated quantity of hydrochloric acid, and evaporating over sulphuric acid. F. Ullik found that the *henicosihydrate* furnishes prismatic crystals which V. von Zepharovich regarded as monoclinic with the axial ratios $a:b:c=1·840:1:—$, and $\beta=93° 32·5'$. When kept for some time, the crystals become turbid and wax-like. The crystals dissolve slowly but copiously in water, and they can be recovered from the soln. unchanged. F. Ullik obtained the *dodecahydrate* by evaporating on a water-bath the clear liquid from a soln. of normal sodium molybdate mixed with the theoretical quantity of hydrochloric acid. The white crystalline powder is dried between bibulous paper; it is sparingly soluble in water. A. Rosenheim and I. Davidsohn prepared the heptahydrate, but A. Rosenheim and J. Felix showed that it is probably the *hexahydrate*, $Na_2Mo_{10}O_{31}.6H_2O$. It was obtained by the prolonged heating in a closed vessel at 40° of a soln. of a mol of sodium molybdate and 2 mols of hydrochloric or nitric acid; A. Rosenheim and J. Felix also obtained it by boiling a soln. of the henacosihydrate. The salt separates in microscopic, six-sided prisms, which are only sparingly soluble in cold or hot water; a sat. soln. at 100° contains 0·842 per cent. $Na_2Mo_{10}O_{31}$. The dodecahydrate of F. Ullik may be the partially dehydrated henacosihydrate.

According to A. Rosenheim and I. Davidsohn, and A. Rosenheim and J. Felix, when a soln. of a mol of normal potassium molybdate and 2 mols of hydrochloric acid is heated for a long time in a closed vessel at 40°, a microcrystalline powder of **potassium decamolybdate,** $K_2O.10MoO_3.9H_2O$, separates out. The *enneahydrate* is sparingly soluble in water; at 100°, the soln. contains 0·682 per cent. of $K_2Mo_{10}O_{31}$. If a cold, conc. aq. soln. of normal potassium molybdate be mixed with an eq. amount of hydrochloric acid, it deposits microscopic six-sided prisms of the *pentadecahydrate*, which is fairly soluble in cold water. If the soln. be warm, the less soluble enneahydrate is formed. The facts do not justify the assumption suggested by A. Rosenheim and J. Felix that the easily- and the sparingly-soluble forms are polymeric; they are explained by the existence of hydrates of different solubilities.

The individuality of F. Ephraim and H. Herschfinkel's *rubidium henamolybdate*, $Rb_2O.11MoO_3.5·5H_2O$, obtained from mixtures of rubidium tetramolybdate and nitric acid, has not been established; similar remarks apply to their *rubidium tridecamolybdate*, $Rb_2O.13MoO_3.4H_2O$.

F. Parmentier reported crystals of **potassium aluminium decamolybdate,** $2K_2O.Al_2O_3.10MoO_3.15H_2O$, to be formed by heating aluminium hydroxide with potassium dimolybdate in a sealed tube at 150°. A. Meinhard prepared **sodium ceridecamolybdate,** $4Na_2O.CeO_2.10MoO_3.5H_2O$; **guanidinium thoridecamolybdate,** $4(CN_3H_6)_2O.ThO_2.10MoO_3$; and **ammonium manganous decamolybdate,** $3(NH_4)_2O.2MnO.10MoO_3.14H_2O$, by the action of a manganous salt on ammonium paramolybdate.

D. N. Artemeéff, and M. K. Eliaschevitsch described the rhombic, prismatic crystals of **ammonium cobaltic decamolybdate,** $3(NH_4)_2O.Co_2O_3.10MoO_3.10H_2O$; and of those of **potassium cobaltic decamolybdate,** $3K_2O.Co_2O_3.10MoO_3.10H_2O$. E. Marckwald obtained **ammonium nickelous decamolybdate,** $3(NH_4)_2O.2NiO.10MoO_3.14H_2O$, by mixing a hot soln. of ammonium paramolybdate and nickelous chloride, and, after the nickelous molybdate has separated, evaporating over sulphuric acid.

REFERENCES.

[1] A. Rosenheim, *Ber.*, **36**. 752, 1903; *Zeit. anorg. Chem.*, **15**. 180, 1897; A. Rosenheim and J. Felix, *ib.*, **79**. 292, 1913; J. Felix, *Zur Kenntnis einiger Polymolybdänate und des Molybdänsauredihydrats*, Berlin, 1912; F. Mylius, *Ber.*, **36**. 638, 1903; P. Klason, *ib.*, **34**. 153, 1901; G. Wempe, *Beiträge zur Kenntnis der Molybdate*, München, 1911; *Zeit. anorg. Chem.*, **78**. 298, 1912; F. Ullik, *Sitzber. Akad. Wien*, **55**. 767, 1867; **60**. 295, 1869; *Liebig's Ann.*, **144**. 204, 320, 1867; **153**. 373, 1870; V. von Zepharovich, *Sitzber. Akad. Wien*, **58**. 112, 1868; D. Asch, *Zur Kenntnis der Schwefligmolybdate*, Berlin, 1902; M. Brand, *Ueber Molybdate, Sulfomolybdate und Phosphormolybdate des Lithiums*, Bern, 1905; F. Ephraim and M. Brand, *Zeit. anorg. Chem.*, **64**. 258, 1909; A. Lancien, *Compt. Rend.*, **144**. 1434, 1907; *Bull. Sci. Pharm.*, **15**. 132, 1908; E. Marckwald, *Ueber die Molybdate des Kobalts, Nickels, Mangans, Eisens, Aluminiums, und Chroms*, Berlin, 1895; S. J. Diatschkovsky and A. V. Dumansky, *Journ. Russ. Phys. Chem. Soc.*, **58**. 630, 1926; A. Meinhard, *Zur Kenntnis der Heteropolymolybdate des Mangans und einiger vierwertiger Elemente*, Berlin, 1928.

[2] L. F. Svanberg and H. Struve, *Svenska Akad. Handl.*, **1**. 9, 1848; *Journ. prakt. Chem.*, (1), **44**. 257, 1848; *Phil. Mag.*, (3), **33**. 409, 524, 1848; R. D. Hall, *Journ. Amer. Chem. Soc.*, **29**, 690, 1907; E. Marckwald, *Ueber die Molybdate des Kobalts, Nickels, Mangans, Eisens, Aluminiums, und Chroms*, Berlin, 1895.

[3] J. Felix, *Zur Kenntnis einiger Polymolybdänate und des Molybdänsauredihydrats*, Berlin, 1912; A. Rosenheim and J. Felix, *Zeit. anorg. Chem.*, **79**. 292, 1913; A. Rosenheim and I. Davidsohn, *ib.*, **37**. 322, 1903; P. Klason, *Ber.*, **34**. 153, 1901; F. Ullik, *Sitzber. Akad. Wien*, **55**. 767, 1867; **60**. 295, 1869; *Liebig's Ann.*, **144**. 204, 320, 1867; **153**. 373, 1870; F. Ephraim and H. Herschfinkel, *Zeit. anorg. Chem.*, **64**. 266, 1909; H. Herschfinkel, *Ueber Molybdate, Sulfomolybdate, Phosphor- und Arseno-molybdate des Rubidiums und Cæsiums*, Bern, 1907; F. Parmentier, *Compt. Rend.*, **94**. 1713, 1882; E. Marckwald, *Ueber die Molybdate des Kobalts, Nickels, Mangans, Eisens, Aluminiums, und Chroms*, Berlin, 1895; M. K. Eliaschevitsch, *Ann. Inst. Mines. St. Petersburg*, **2**. 345, 1910; D. N. Arteméeff, *ib.*, **2**. 275, 1910; A. Meinhard, *Zur Kenntnis der Heteropolymolybdate des Mangans und einiger vierwertiger Elemente*, Berlin, 1928; V. von Zepharovich, *Sitbzer. Akad. Wien*, **58**. 112, 1868.

§ 15. The Dodeca-, and Higher Molybdates

G. Jander and A. Winkel[1] found the range of stability of **sodium dodecamolybdate,** $Na_3(H_7Mo_{12}O_{41})$.aq., to correspond with $[H^{\cdot}]=10^{-1\cdot5}$ to $10^{-0\cdot9}$; and they gave 0·20 for the diffusion coeff. of the anion. G. Wempe treated a soln. of ammonium tetramolybdate with calcium chloride in eq. proportions, and evaporated the liquid on a water-bath. The resulting monoclinic or triclinic prisms were regarded as **calcium dodecamolybdate,** $CaMo_{12}O_{37}.23H_2O$. The crystals effloresce in air; they are almost insoluble in cold water, but readily soluble in hot water.

R. D. Hall prepared crystals of **ammonium aluminium dodecamolybdate,** $3(NH_4)_2O.Al_2O_3.12MoO_3.19H_2O$, or $(NH_4)_3Al(Mo_2O_7)_3.9\frac{1}{2}H_2O$, by boiling 100 grms. of ammonium paramolybdate with 33 grms. of aluminium sulphate in 1·5 litres of water, and cooling the hot liquid. H. Struve regarded it as a decahydrate. The salt was also prepared by E. Marckwald. Attempts by A. Rosenheim and H. Schwer to resolve the ammonium strychnine salt into optical isomerides failed. The electrical conductivity, λ, of $\frac{1}{3}(NH_4)_3H_6[Al(MoO_4)_6].7H_2O$, in v litres of water, at 25°, is:

v . .	32	64	128	256	512	1024
λ . .	100·56	108·5	116·0	122·9	132·8	143·3

J. G. Gentele prepared **sodium aluminium dodecamolybdate,** $Na_3Al(Mo_2O_7)_3.11H_2O$, by treating a soln. of potash-alum with sodium molybdate in excess. The needle-like crystals are easily soluble in water; they effloresce in air; and lose about half their water of crystallization over sulphuric acid. The salt melts when heated, and the cold crystalline mass dissolves slowly in hydrochloric acid. H. Struve boiled freshly-precipitated aluminium hydroxide for many hours with a soln. of potassium trimolybdate, replacing water as it evaporates. The hot liquid is filtered and cooled for the crystals of **potassium aluminium dodecamolybdate,** $3K_2O.Al_2O_3.12MoO_3.20H_2O$, or $K_3Al(Mo_2O_7)_3.10H_2O$. The same salt was obtained by treating a soln. of potash-alum with a normal molybdate—say, magnesium molybdate; and R. D. Hall also obtained it by the action of aluminium sulphate or potash-alum on a molybdate. H. Struve said that the hot soln. furnishes four-sided plates on cooling. The crystals are stable in air; 100 parts of water at 17° dissolve 0·025 part of the salt. The original salt can be obtained by crystallization from the aq. soln. The salt melts at a red-heat, and when cold, the mass is sparingly soluble in water and acids. A. Rosenheim and H. Schwer discussed the hypotheses as to their constitution (i) that they are constituted $R_3[Al(Mo_2O_7)_3].nH_2O$, or $R_3[Al(H_2O)_2(Mo_2O_7)_3].(n-2)H_2O$; or (ii) that they are derivatives of the nonavalent (AlO_6)-radicle. The way the potassium salt loses water, when it is heated, agrees with the hypotheses that the potassium salt is constituted in accord with $K_3H_6[Al(MoO_4)_6].7H_2O$. The percentage loss of water is as follows:

	100°	110°	120°	130°	150°	170°	Red-heat
Loss .	9·90	10·22	10·32	10·32	10·54	11·47	14·68
	$7H_2O$						$10H_2O$

The electrical conductivity, λ, of an eq., $\frac{1}{3}K_3H_6[Al(MoO_4)_6].7H_2O$, in v litres of water, at 25°, is:

v . .	32	64	128	256	512	1024
λ . .	97·42	105·93	113·34	121·04	130·97	140·02

R. D. Hall reported that if an eq. amount of silver nitrate be added to an alkali aluminium dodecamolybdate, only part of the alkali is replaced, but if an excess of the silver salt be employed, **silver aluminium oxydodecamolybdate,** $Ag_2O.Ag_6Al_2(Mo_2O_7)_6.16H_2O$, is formed. If a still larger excess of silver salt be used, **silver aluminium dioxymolybdate,** $2Ag_2O.Ag_6Al_2(Mo_2O_7)_6.nH_2O$, is produced; **barium aluminium oxydodecamolybdate,** $BaO.Ba_3Al_2(Mo_2O_7)_6.14H_2O$, is formed by boiling barium chloride with a soln. of the salt $K_3Al(Mo_2O_7)_3.10H_2O$; and also **ammonium barium aluminium oxydodecamolybdate,** $0·85(NH_4)_2O.2·15BaO.Al_2O_3.12MoO_3.20H_2O$, by the action of barium chloride on the ammonium salt. R. D. Hall prepared **lead aluminium oxydodecamolybdate,** $PbO.Pb_3Al_2(Mo_2O_7)_6.21H_2O$, as in the case of the corresponding silver salt.

G. A. Barbieri prepared a series of **ceriododecamolybdates** of the general formula $R_8[Ce(Mo_2O_7)_6].nH_2O$, derived from the ceridodecamolybdic acid, $H_8[Ce(Mo_2O_7)_6]$. These salts are stable towards hydrogen dioxide, and give a precipitate with oxalic acid only after prolonged boiling. Yellow crystals of **ammonium ceric dodecamolybdate,** $(NH_4)_8[Ce(Mo_2O_7)_6].8H_2O$, were obtained by adding a soln. of conc. ammonium nitrate to a soln. of ammonium paramolybdate, and the product, when treated with dil. sulphuric acid furnished pale yellow crystals of **ammonium ceric dihydrododecamolybdate,** $(NH_4)_6H_2[Ce(Mo_2O_7)_6].10H_2O$; A. Meinhard obtained **sodium ceric dodecamolybdate,** $4Na_2O.CeO_2.1M2oO_3.6H_2O$; while G. A. Barbieri obtained orange-yellow, crystals of **silver ceric dodecamolybdate,** $Ag_8[Ce(Mo_2O_7)_6]$; and yellow crystals of *aniline ceric dodecamolybdate* were prepared by double decomposition with the ammonium salt and silver nitrate.

E. Péchard prepared a series of complex **titanidodecamolybdates,** of the general formula $R_8[Ti(Mo_2O_7)_6].nH_2O$. He obtained **titanidodecamolybdic acid,** $H_8[Ti(Mo_2O_7)_6].18H_2O$, by adding hydrochlorous acid to mercurous titanimolybdate, or by agitating with ether an aq. soln. of the ammonium salt acidified with hydrochloric acid, and allowing the heavier liquid to evaporate spontaneously. The golden-yellow octahedra melt at 60°, and are very soluble in water. He prepared **ammonium titanidodecamolybdate,** $2(NH_4)_2O.TiO_2.12MoO_3.10H_2O$, *i.e.* $(NH_4)_4H_4[Ti(Mo_2O_7)_6].8H_2O$, by adding a soln. of ammonium fluotitanate to a soln. of ammonium molybdate until the yellow colour no longer increases in intensity, and then adding hydrochloric acid. The salt is insoluble in soln. of ammonium salts, but dissolves in water and in acids. It furnishes yellow octahedra which act on polarized light. If a hot, conc. soln. of this salt be treated with potassium chloride and allowed to cool, efflorescent prisms of **potassium titanidododeca-**

molybdate, $K_4H_4[Ti(Mo_2O_7)_6].14H_2O$, are deposited. If a mercurous salt soln. be added to an aq. soln. of one of these two salts, **mercurous titanidodecamolybdate** is formed. E. Péchard prepared **zirconidodecamolybdates,** $R_8[Zr(Mo_2O_7)_6].nH_2O$, in an analogous manner; **ammonium zirconidodecamolybdate,** $(NH_4)_4H_4[Zr(Mo_2O_7)_6].8H_2O$, yields brown octahedra; and **potassium zirconidodecamolybdate,** $K_4H_4[Zr(Mo_2O_7)_6].16H_2O$, brown prisms.

G. A. Barbieri obtained a series of **thoridodecamolybdates,** $R_8[Th(Mo_2O_7)_6].nH_2O$. They do not give a precipitate with oxalic acid in the cold, but, on boiling, thorium oxalate is slowly deposited. When 10 grms. of anhydrous thorium sulphate dissolved in 200 c.c. of water are added to 250 c.c. of a 30 per cent. soln. of ammonium heptamolybdate, a white precipitate of **ammonium thoridodecamolybdate,** $(NH_4)_8[Th(Mo_2O_7)_6].8H_2O$, is deposited. A. Meinhard also prepared this salt. G. A. Barbieri showed that if the nitric or hydrochloric acid soln. of this salt be treated with a conc. soln. of an ammonium salt, **ammonium dihydrothoridodecamolybdate,** $(NH_4)_6H_2[Th(Mo_2O_7)_6].11H_2O$, is deposited; similarly with **sodium thoridodecamolybdate,** $Na_8[Th(Mo_2O_7)_6].15H_2O$, which forms needle-like crystals, and with **sodium dihydrothoridodecamolybdate,** $Na_6H_2[Th(Mo_2O_7)_6].17H_2O$—A. Meinhard also prepared the former salt. According to G. A. Barbieri, the addition of silver nitrate to a soln. of one of these salts furnishes **silver thoridodecamolybdate,** $Ag_8[Th(Mo_2O_7)_6]$, as a white powder. Precipitates of **magnesium thoridodecamolybdate,** and of **zinc thoridodecamolybdate** are similarly produced. A. Rosenheim obtained **ammonium stannidodecamolybdate,** $(NH_4)_8[Sn(Mo_2O_7)_6].20H_2O$, as a microcrystalline, white powder, by the action of a soln. of ammonium paramolybdate on ammonium chlorostannate. A. Meinhard also prepared **ammonium hydrostannidodecamolybdate,** $(NH_4)_3H_5[Sn[Mo_2O_7)_6].4H_2O$, which was regarded as a salt of **stannidodecamolybdic acid,** $H_8[Sn(Mo_2O_7)_6]$.

A series of complex **chromidodecamolybdates,** $3R_2O.Cr_2O_3.12MoO_3.nH_2O$, or $R_3[Cr(Mo_2O_7)_3].nH_2O$, was prepared by H. Struve, E. Marckwald, and R. D. Hall. H. Struve prepared rose-red plates of **ammonium chromidodecamolybdate,** $3(NH_4)_2O.Cr_2O_3.12MoO_3.20H_2O$, or $(NH_4)_3H_6[Cr(MoO_4)_6].7H_2O$, by boiling a soln. of ammonium trimolybdate with hydrated chromic oxide; and R. D. Hall, by boiling a soln. of ammonium chrome-alum and ammonium paramolybdate. E. Marckwald obtained the hexacosihydrate. A. Rosenheim and H. Schwer prepared two guanidine salts; and an attempt to resolve the ammonium strychnine salt into optical isomerides failed. Similarly with the rose-red plates of **potassium chromidodecamolybdate,** $3K_2O.Cr_2O_3.12MoO_3.20H_2O$, or $K_3H_6[Cr(MoO_4)_6].7H_2O$. The salt undergoes no change on dialysis. At 17°, 100 grms. of water dissolve 2·6 grms. of the salt. The percentage loss in weight is:

	100°	110°	120°	130°	150°	170°	Red-heat
Loss .	9·66	10·04	10·08	10·08	10·34	12·71	14·39

A. Rosenheim and H. Schwer found that the electrical conductivity, λ, of a soln. of an eq. of the normal salt, $\frac{1}{3}K_3H_6[Cr(MoO_6)].7H_2O$, in v litres of water, at 25°, is:

v . .	32	64	128	256	512	1024
λ . .	97·91	106·6	114·3	121·8	131·2	140·3

If the potassium salt be crystallized from soln. containing varying proportions of potassium hydroxide a series of **potassium chromioxydodecamolybdates** is formed, *viz.* 7 : 2 : 24 : 32 ; 4 : 1 : 12 : 15 ; and 4 : 1 : 12 : 20. A. Rosenheim and H. Schwer consider that these products are mixtures. H. Struve obtained **sodium chromidodecamolybdate,** $3Na_2O.Cr_2O_3.12MoO_3.21H_2O$, as in the case of ammonium salt. By adding the respective salts of the base to a soln. of potassium chromidodecamolybdate, R. D. Hall prepared **silver chromidodecamolybdate,** $5Ag_2O.Cr_2O_3.12MoO_3.17H_2$, by using an excess of silver nitrate, if otherwise, **potassium silver chromidodecamolybdate,** $2\frac{1}{4}Ag_2O.\frac{3}{4}K_2O.Cr_2O_3.12MoO_3.18H_2O$, is formed; **barium chromioxydodecamolybdate,** $4BaO.Cr_2O_3.12MoO_3.15H_2O$, as well as the hexadecahydrate is formed by using an excess of barium chloride, if otherwise, **potassium barium chromidodecamolybdate,** $2{\cdot}15BaO.0{\cdot}85K_2O.Cr_2O_3.12MoO_3.20H_2O$; and with an ammonium salt, **ammonium barium chromidodecamolybdate,** $2BaO.(NH_4)_2O.Cr_2O_3.12MoO_3.20H_2O$; by using a mixture of an excess of barium chloride and barium hydroxide, in the cold, **barium chromidioxydodecamolybdate,** $5BaO.Cr_2O_3.12MoO_3.12H_2O$, is formed; A. Rosenheim and H. Schwer reported the formation of $Ba_2H_5[Cr(MoO_4)_6].5H_2O$; and they consider that the basic salts here described are impure normal salts. R. D. Hall found that an excess of mercurous nitrate furnishes **mercurous chromipentoxydodecamolybdate,** $8Hg_2O.Cr_2O_3.12MoO_3.16H_2O$; with the theoretical amount of lead nitrate, **lead chromioxydodecamolybdate,** $4PbO.Cr_2O_3.12MoO_3.24H_2O$, was formed, and with five times this amount of lead nitrate, the docosihydrate was produced. If the mercurous salt be decomposed with dil. hydrochloric acid, and the filtrate evaporated to a small bulk over a water-bath, and then to dryness, over sulphuric acid, **chromidodecamolybdic acid,** $Cr_2O_3.12MoO_3.28H_2O$, is formed as a green powder.

A. Rosenheim and J. Pinsker prepared **ammonium manganous dodecamolybdate,** $3(NH_4)_2O.2MnO.12MoO_3.22H_2O$; and by the action of salts of tervalent manganese on alkali paramolybdates, A. Meinhard obtained **ammonium manganic dodecamolybdate,** $4(NH_4)_2O.Mn_2O_3.12MoO_3.9H_2O$, and also **potassium manganic dodecamolybdate,** $4K_2O.Mn_2O_3.12MoO_3.30H_2O$. These salts are analogous with the corresponding $4R_2O.Fe_2O_3.12WO_3.nH_2O$.

F. Zambonini and V. Caglioti prepared **ammonium manganic tridecamolybdate,** $4(NH_4)_2O.Mn_2O_3.13MoO_3.9H_2O$, where Mn_2O_3 may also be regarded as $MnO.MnO_2$. This salt is considered to be one member of a series of isomorphous complex salts of the type: $[Mn^{\cdot\cdot\cdot\cdot}(Mo_2O_7)_6]R_8Mn^{\cdot\cdot}MoO_4.9H_2O$, where R is the third basal element —*vide supra*, permanganitomolybdates. The ammonium salt is produced by adding 100 c.c. of a conc. soln. of manganous chloride (75 grms. $MnCl_2$ per 1000 c.c. of water) to 1800 c.c. of a hot soln. of ammonium paramolybdate (250 grms. of salt per litre), and then adding 800 c.c. of hydrogen dioxide. The soln. is filtered whilst hot, and on cooling red crystals are deposited. The crystals were decanted, washed with water, and dried in air on a porous tile. The triclinic crystals have uniaxial birefringence without optical anomalies, they are pleochoric, and have a sp. gr. 3·028. By adding potassium chloride to a soln. of the ammonium salt at 80°, isomorphous orange-red crystals of **potassium manganic tridecamolybdate,** $4K_2O.Mn_2O_3.13MoO_3.9H_2O$, of sp. gr. 3·43, were produced. The crystals have a positive, uniaxial birefringence without optical anomalies, and they are pleochroic. The corresponding **rubidium manganic tridecamolybdate,** $4Rb_2O.Mn_2O_3.13MoO_3.9H_2O$, was obtained in a similar manner and furnished orange-red, strongly pleochroic crystals. This salt was probably also made by H. Struve in 1854. F. Zambonini and V. Caglioti found that if sodium chloride is employed in place of potassium chloride, the soln. after standing some months deposits orange-red, pleochroic, monoclinic crystals of **sodium ammonium manganic tridecamolybdate,** $2Na_2O.2(NH_4)_2O.Mn_2O_3.13MoO_3.9H_2O$. A boiling soln. of the alkali salt to which nickel sulphate and ammonium persulphate are added, yields purple-black triclinic crystals of **ammonium nickelic tridecamolybdate,** $[Ni^{\cdot\cdot\cdot\cdot}(Mo_2O_7)_6](NH_4)_8NiMoO_4.9H_2O$, isomorphous with the corresponding manganic salt. The corresponding **magnesium, cupric, and cadmium salts** appear as isomorphous mixtures with the ammonium salt. The corresponding **chromic and cobaltic salts** were obtained, but no solid soln. with the manganic salt could be prepared. If the potassium, or ammonium, or sodium manganic salt is treated with barium chloride, at 80°, rose-yellow **barium manganic dodecamolybdate,** $Ba_4[Mn(Mo_2O_7)_6].nH_2O$, is formed; and with the potassium manganic salt and silver nitrate, flesh-coloured crystals of **silver manganic dodecamolybdate,** $Ag_8[Mn(Mo_2O_7)_6].nH_2O$, are produced.

According to E. Marckwald, **ammonium ferric dodecamolybdate,** $3(NH_4)_2O.Fe_2O_3.12MoO_3.20H_2O$, is produced by treating ferric chloride with ammonium paramolybdate. The salt $Fe_2O_3.5MoO_3.nH_2O$ is first deposited, and afterwards white plates of the complex salt, which are decomposed by water. The same salt was prepared by H. Struve, and R. D. Hall. The latter gave $19H_2O$ for the proportion of combined water; and A. Rosenheim and H. Schwer represented it by $(NH_4)_3H_6[Fe(MoO_4)_6].7H_2O$. R. D. Hall also obtained **potassium ferric dodecamolybdate,** $3K_2O.Fe_2O_3.12MoO_3.20H_2O$. A. Rosenheim and H. Schwer represented it by $K_3H_6[Fe(MoO_4)_6].7H_2O$; they found the percentage loss of water:

	100°	110°	120°	130°	150°	170°	Red-heat
Loss . .	9·70	10·01	10·06	10·06	10·40	11·70	14·28
	$7H_2O$						$10H_2O$

They found the conductivity, λ of $K_3H_6[Fe(MoO_4)_6].7H_2O$ in v litres of water, at 25°,

v . .	32	64	128	256	512	1024
λ . .	97·88	103·0	115·64	124·11	136·9	153·75

E. Marckwald prepared **sodium cobaltous dodecamolybdate,** $Na_2O.CoO.12MoO_3.14H_2O$, by heating a soln. of a mol of sodium paramolybdate with 3 mols of cobaltic chloride. The violet precipitate does not appear homogeneous under the microscope and is thought to be a mixture of sodium trimolybdate and normal cobaltous molybdate. E. Marckwald also obtained $3Na_2O.2CoO.12MoO_3.27H_2O$, or $4CoO.6Na_2O.25MoO_3.54H_2O$, from a soln. of eq. quantities of sodium tetramolybdate and cobaltous chloride. The yellowish-red crystals may be a mixture of $2(2CoO.5MoO_3)+3(2Na_2O.5MoO_3)$. He also reported a yellowish-red crystalline mass of $4Na_2O.6CoO.25MoO_3.68H_2O$, by evaporating over sulphuric acid the filtrate from a soln. of a mol of sodium paramolybdate, and 3 mols of cobaltous chloride.

G. A. Barbieri[2] prepared a couple of complex rhodic molybdates analogous to to be those obtained with tervalent aluminium, chromium, iron, and cobalt. These are: **ammonium rhodic dodecamolybdate,** $3(NH_4)_2O.Rh_2O_3.12MoO_3.20H_2O$, or $(NH_4)_3H_6[Rh(MoO_4)_6].7H_2O$, in minute, yellow plates; and **potassium rhodic dodecamolybdate,** $3K_2O.Rh_2O_3.12MoO_3.20H_2O$, or $K_3H_6[Rh(MoO_4)_6].7H_2O$, also in small yellow plates.

E. Marckwald[3] prepared **nickel tetradecamolybdate,** $5NiO.14MoO_3.70H_2O$, from the mother-liquor of the 8 : 6 : 31-molybdate. The green crystals are sparingly soluble in cold water and easily soluble in hot water. When recrystallized from water, the 57-hydrate is produced. G. Wempe prepared **lithium hexadecamolybdate,** $Li_2Mo_{16}O_{49}.9.5H_2O$, by treating a mol of normal lithium molybdate with 1·5 mols of hydrochloric acid. The precipitate first formed redissolves, and the soln. deposits, on standing, rhombohedral crystals which are probably triclinic. They dissolve in warm water; and melt when strongly heated. L. F. Svanberg and H. Struve described a commercial sodium molybdate which approximated **sodium hexadecamolybdate,** $Na_2O.16MoO_3.9H_2O$; and F. Ullik prepared it by boiling for a long time a rather conc. soln. of sodium molybdate with nitric acid of sp. gr. 1·5. The composition of the white precipitate seemed to be independent of the relative proportions of the constituents. It should be washed with dil. nitric acid because it is peptized by water alone. When the salt is treated with sodium carbonate, it forms the octomolybdate. F. Ephraim and H. Herschfinkel boiled an acid cæsium molybdate with nitric acid of sp. gr. 1·20 and obtained a yellow, amorphous substance to which the formula for **cæsium hexadecamolybdate,** $Cs_2O.16MoO_3.8H_2O$, was assigned. F. Ullik regarded this product as $2Na_2O.16MoO_3.8H_2O$, a polymerized form of the octohydrate. F. Ullik also prepared **magnesium hexadecamolybdate,** $MgO.16MoO_3.30H_2O$, in an analogous manner. The microscopic crystals are sparingly soluble in cold water, but easily soluble in hot water. The salt loses water when heated, and melts with decomposition at a dull red-heat. If a mixture of eq. proportions of soln. of ammonium paramolybdate and nickelous chloride be evaporated in the cold, **ammonium nickelous hexadecamolybdate,** $6(NH_4)_2O.3NiO.16MoO_3.29H_2O$, is formed in green crystals, which are sparingly soluble in cold and readily soluble in hot water without decomposition.

E. Marckwald also evaporated a soln. with a great excess of nickelous chloride and obtained **ammonium nickelous henitricontamolybdate,** $8(NH_4)_2O.6NiO.31MoO_3.63H_2O$; and the mother-liquor from the decamolybdate furnishes **ammonium nickelous tetratricontamolybdate,** $3(NH_4)_2O.9NiO.34MoO_3.120H_2O$. R. D. Hall prepared **ammonium nickelous hexadecamolybdate,** $5(NH_4)_2O.3NiO.16MoO_3.16H_2O$, by heating a soln. of nickelous sulphate and ammonium molybdate with hydrogen dioxide; and also **potassium nickelous hexadecamolybdate,** $5K_2O.3NiO.16MoO_3.21H_2O$, from a soln. of potassium paramolybdate and nickelous sulphate alone or in the presence of hydrogen dioxide, chlorine, and bromine.

According to G. A. Barbieri,[4] rhodium forms complex molybdates analogous to the tervalent aluminium, iron, chromium, and cobalt complexes. Thus, **ammonium rhodic dodecamolybdate,** $3(NH_4)_2O.Rh_2O_3.12MoO_3.20H_2O$, forms yellow laminæ, and similarly with **potassium rhodic dodecamolybdate,** $3(NH_4)_2O.Rh_2O_3.12MoO_3.20H_2O$.

G. Canneri[5] obtained a series of hypomolybdatomolybdates by heating for a long time a mixture of hydroxylamine chloride and a soln. of an alkali molybdate. The salts are constituted:

$$R_4[(Mo_2O_5)(Mo_2O_7)_2].nH_2O.$$

The red salt, **ammonium hypomolybdatomolybdate,** $2(NH_4)_2O.Mo_2O_5.4MoO_3.8H_2O$, forms a red soln. with water; **sodium hypomolybdatomolybdate,** $2Na_2O.Mo_2O_5.4MoO_3.10H_2O$, is brick-red; red **potassium hypomolybdatomolybdate,** $2K_2O.Mo_2O_5.4MoO_3.5H_2O$, forms an orange-red soln. with water.

C. G. Grossup[6] prepared germanomolybdic acid, $H_8[Ge(Mo_2O_7)_6].25H_2O$, analogous to silicomolybdic acid.

Five grms. of germanic oxide were dissolved in 200 ml. of water containing 7 grms. of sodium hydroxide, and the soln. brought to boiling, whereupon 70 grms. of molybdic oxide were slowly added with stirring. Rapid dissolution of the molybdic oxide took place until about half the amount had been added. Almost complete precipitation occurred at this point, followed by re-solution with continued addition of the molybdic oxide. An intense yellow colour developed after this mid-point of reaction. Gentle boiling was continued for five minutes, the soln. filtered and allowed to cool. Several hundred ml. of ether were added, followed by an excess of cold $9N$-H_2SO_4. An intermediate turbidity disappeared when sufficient acid had been added. Heavy yellow oily drops separated and settled, forming the third layer common to such extractions. This lower layer—an ether soln. of the complex acid—was removed and evaporated at 40°. After powdering, the residue was dissolved in a small vol. of water and the extraction with ether and sulphuric acid repeated. The ether was removed as before, the residue dissolved in water, the soln. filtered, and then allowed to crystallize at room temp. (18°–28°). The major portion of mother-liquor was removed by filtration and the crystals dried as rapidly as possible by pressing between filter paper, after which they were kept in tightly stoppered weighing bottles or weighed out at once for analysis. In spite of the high solubility, the soln. crystallized well.

A guanidine salt, $(CN_3H_5)_4H_4[Ge(Mo_2O_7)_6]$, was prepared.

REFERENCES.

[1] G. Wempe, *Beiträge zur Kenntnis der Molybdate*, München, 1911; *Zeit. anorg. Chem.*, **78**. 298, 1912; E. Marckwald, *Ueber die Molybdate des Kobalts, Nickels, Mangans, Eisens, Aluminiums, und Chroms*, Berlin, 1895; H. Struve, *Bull. Acad. St. Petersburg*, (2), **12**. 142, 1854; *Journ. prakt. Chem.*, (1), **61**. 453, 1854; J. G. Gentele, *Journ. prakt. Chem.*, (1), **81**. 413, 1860; R. D. Hall, *Journ. Amer. Chem. Soc.*, **29**. 690, 1907; H. Schwer, *Ueber neunbasische Heteropolysäuren*, Berlin, 1914; A. Rosenheim and H. Schwer, *Zeit. anorg. Chem.*, **89**. 224, 1914; A. Rosenheim and J. Pinsker, *ib.*, **96**. 149, 1916; A. Rosenheim, *ib.*, **96**. 139, 1916; G. A. Barbieri, *Atti Accad. Lincei*, (5), **22**. i, 781, 1913; (5), **23**. i, 805, 1914; E. Péchard, *Compt. Rend.*, **117**. 788, 1893; N. S. Kurnakoff, *Chem. Ztg.*, **14**. 113, 1900; C. Friedheim and F. Keller, *Ber.*, **39**. 4301, 1906; A. Meinhard, *Zur Kenntnis der Heteropolymolybdate des Mangans und einiger vierwertiger Elemente*, Berlin, 1928; F. Zambonini and V. Caglioti, *Gazz. Chim. Ital.*, **59**. 400, 1929; *Atti Accad. Napoli*, **33**. 181, 1927; G. Jander and A. Winkel, *Zeit. phys. Chem.*, **149**. 97, 1930.

[2] G. A. Barbieri, *Atti Accad. Lincei*, (5), **23**. i, 334, 1914.

[3] L. F. Svanberg and H. Struve, *Svenska Akad. Handl.*, **1**. 9, 1848; *Journ. prakt. Chem.*, (1),

44. 257, 1848; *Phil. Mag.*, (3), **33.** 409, 524, 1848; F. Ullik, *Sitzber. Akad. Wien*, **55.** 767, 1867; **60.** 295, 1869; *Liebig's Ann.*, **144.** 204, 320, 1867; **153.** 373, 1870; F. Ephraim and H. Herschfinkel, *Zeit. anorg. Chem.*, **64.** 266, 1909; H. Herschfinkel, *Ueber Molybdate, Sulfomolybdate, Phosphor- und Arseno-molybdate des Rubidiums und des Cæsiums*, Bern, 1907; G. Wempe, *Beiträge zur Kenntnis der Molybdate*, München, 1911; *Zeit. anorg. Chem.*, **78.** 298, 1912; E. Marckwald, *Ueber die Molybdate des Kobalts, Nickels, Mangans, Eisens, Aluminiums, und Chroms*, Berlin, 1895; R. D. Hall, *Journ. Amer. Chem. Soc.*, **29.** 690, 1907.

[4] G. A. Barbieri, *Atti Accad. Lincei*, (5), **23.** i, 334, 1914.

[5] G. Canneri, *Gazz. Chim. Ital.*, **57.** 872, 1927.

[6] C. G. Grossup, *Journ. Amer. Chem. Soc.*, **52.** 5154, 1930.

§ 16. Permolybdic Acid and Permolybdates

R. Brandes,[1] G. C. Wittstein, and L. F. Svanberg and H. Struve reported *hyperacid molybdates*, but they probably meant polymolybdates and not **permolybdates** as these terms are understood to-day. G. Werther observed that acid soln. of the molybdates, when treated with hydrogen dioxide, give a yellow coloration which, according to C. Bärwald, is not extracted by ether, and which, according to G. Denigès, is not affected by heating the liquid. The analytical possibilities of the reaction were discussed by L. Schönn, A. Weller, L. Crismer, G. Denigès, A. C. Stark, etc. T. Fairley showed that the colour is due to the formation of permolybdic acid or acids in soln. The yellow, or orange-yellow acid soln. gradually deposits an insoluble yellow compound. E. Péchard said that **permolybdic acid,** $HMoO_4$, or $Mo_2O_7.5H_2O$, is isolated by decomposing the barium salt with sulphuric acid; by heating dihydrated molybdenum trioxide with a soln. of hydrogen dioxide; or, by the action of hydrogen dioxide on molybdenum, or its blue oxide. If the soln. obtained by one of these methods is evaporated in vacuo at ordinary temp., it yields a yellow, crystalline powder, soluble in water. The aq. soln. can be boiled without decomposition; with hydrochloric acid there is an evolution of chlorine. Reducing agents like stannous chloride and ferrous sulphate first yield molybdenum trioxide, and then the blue oxide. At 100°, the acid loses $4H_2O$, and, at a higher temp., it simultaneously loses both the remaining water and oxygen. The composition of the salts shows that the acid is monobasic, and this is all in agreement with the formula $HMoO_4.2H_2O$. The direct neutralization of permolybdic acid by sodium hydroxide develops $+24{\cdot}2$ Cals., and by potassium hydroxide $+24{\cdot}0$ Cals. The action of sulphuric acid on sodium permolybdate develops $+6{\cdot}9$ Cals., and the result is the same whether the sulphuric acid is added all at once or in successive portions. The whole of the molybdic acid is not displaced. but a very acid molybdate is formed, its formation corresponding with the evolution of 0·6 Cal. The action of hydrogen dioxide on a mixture of sodium molybdate with sulphuric acid in mol. proportion develops $+5{\cdot}4$ Cals., a quantity which may be regarded as the sum of the heat developed by the decomposition of the hydrogen dioxide and that absorbed by the formation of the permolybdate. It follows that the heat of formation of the permolybdate is $-16{\cdot}2$ Cals. The direct neutralization of permolybdic acid develops with sodium hydroxide $+11{\cdot}2$ Cals., and with potassium hydroxide $+11{\cdot}1$ Cals. It follows that permolybdic acid will displace carbonic acid, but is itself displaced by the strong acids. The action of alkaline hydroxides on the permolybdates, with production of molybdates, gives for the heat of formation of permolybdic acid from molybdic acid $-15{\cdot}9$ Cals., a number almost identical with that obtained by the action of hydrogen dioxide. The energy necessary for the formation of the permolybdic acid is derived from the decomposition of the hydrogen dioxide. According to J. Bruhat and H. Dubois, yellow salts of the acid, $Mo_2O_7.H_2O$, or $HMoO_4$, are produced by the action of perborates on molybdates; and, according to F. Fichter and A. Goldach, permolybdic acid is produced by the action of fluorine on a hydrofluoric acid soln. of molybdic acid.

According to W. Muthmann and W. Nagel, the analytical methods employed by E. Péchard are unsatisfactory. What they called *ozomolybdic acid*, $H_2MoO_5.1\frac{1}{2}H_2O$, was obtained by digesting molybdenum trioxide with a 25 per cent.

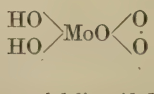
soln. of hydrogen dioxide, on a water-bath, filtering, and concentrating the filtrate under reduced press. The orange-red product is amorphous; it reduces permanganates, silver oxide, and hypochlorites; it liberates halogens from their hydrogen compounds. The salts—ozomolybdates—are obtained by dissolving molybdates in a 25 per cent. soln. of hydrogen dioxide with the aid of heat. They believe that these salts are not true permolybdates, for the heat of the reaction shows that the apparent addition of oxygen to molybdic acid really consists in the replacement of one atom of oxygen by two linked atoms of oxygen as in hydrogen dioxide or ozone. Hence, the proposed term ozomolybdates, and ozomolybdic acid. L. Pissarjewksy, also, repeated E. Péchard's mode of preparing permolybdic acid, and when the ratio of molybdenum to active oxygen in the product was determined by titration with potassium permanganate in sulphuric acid soln., it was found to be 1 : 1 in agreement with **permonomolybdic acid,** $H_2MoO_5.2H_2O$, or $MoO_3.H_2O_2.2H_2O$. J. B. Cammerer also found that when purified molybdenum trioxide is boiled with a soln. of hydrogen dioxide, it gradually dissolves with the evolution of oxygen. When the yellow liquid is evaporated spontaneously, a thickish orange-red mass is obtained, and this can be dried to a yellow powder. The analysis corresponds with $2MoO_3.H_2O.H_2O_2$. The hydrogen dioxide cannot be expelled by heat at 100°. The powder is sparingly soluble in cold water, but is freely soluble in hot water. The compound is not precipitated when the soln. in hot water is cooled. The aq. soln. reacts strongly acid; it combines with acids to form nearly colourless products; and decomposes alkaline carbonates forming colourless salts.

J. Brode measured the distribution of hydrogen dioxide between ether and an acid soln. of molybdate. The result is independent of the amount of hydrogen dioxide and of the conc. of the acid being always in the proportion $MoO_3 : H_2O_2 = 1 : 2$. In the presence of an excess of hydrogen dioxide, the soln. contains $H_2MoO_6 = MoO_2(OOH)_2$; the intensity of the coloration with the gradual addition of hydrogen dioxide reaches a maximum when the ratio is 1 : 1. This is taken to mean that the soln. contains $H_2MoO_5 = MoO_2(OH)(OOH)$. L. Pissarjewsky also found the thermal effect, Q Cals., of dissolving molybdenum trioxide in aq. hydrogen dioxide, to be:

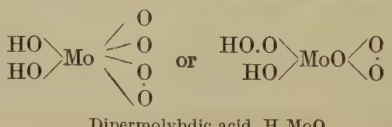
Mols H_2O_2 per mol MoO_3	1	2	3	5
Heat developed, Q	8·08	12·33	12·33	12·44 Cals.

The first reaction is assumed to be $H_2MoO_4 + H_2O_2 = H_2MoO_5 + H_2O + 8084$ cals.; and the second $H_2MoO_5 + H_2O_2 = H_2MoO_6 + H_2O + 4300$ cals. Additions of hydrogen dioxide to the second acid have no thermal effect. Consequently, the heats of formation of the two permolybdic acids are $(H_2MoO_4,O) = 13·516$ Cals.; $(H_2MoO_4,2O) = 30,812$ Cals.; and $(H_2MoO_5,O) = 17·295$ Cals. The heat of neutralization of permolybdic acid, H_2MoO_5, with 2NaOH is 13,248 Cals. A. Mazzucchelli and G. Zangrilli measured the f.p. of the permolybdic acids produced by adding successive quantities of hydrogen dioxide. The results show that the number of dissolved molecules increases only slightly until the ratio $MoO_3 : H_2O_2$ is approximately 1 : 1; and after the formation of H_2MoO_5 is completed a further quantity of hydrogen dioxide enters into combination. Owing to dissociation, and the formation of colloidal complexes, the results are not very reliable. A. Mazzucchelli and C. Barbero found that hydrogen dioxide in a soln. of a mol of MoO_3 in 10 litres of N-H_2SO_4, gives an oxidation potential of 1·008 to 1·025 volts with platinum electrodes.

The general results show that there are two permolybdic acids: **permonomolybdic acid,** H_2MoO_5, or $MoO_3.H_2O_2$, and **perdimolybdic acid,** H_2MoO_6, or $MoO_3.2H_2O_2$, whose constitutions, according to L. Pissarjewsky, can be written:

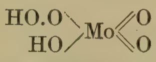


Monopermolybdic acid, H_2MoO_5



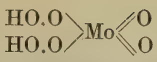
Dipermolybdic acid, H_2MoO_6

They can also be formulated :



$$\begin{matrix} HO.O \\ HO \end{matrix} > Mo < \begin{matrix} O \\ O \end{matrix}$$

Monopermolybdic acid, H_2MoO_5



$$\begin{matrix} HO.O \\ HO.O \end{matrix} > Mo < \begin{matrix} O \\ O \end{matrix}$$

Dipermolybdic acid, H_2MoO_6

According to A. Mazzucchelli and G. Zangrilli, if potassium dihydroarsenatomolybdate be dissolved in water and treated with hydrogen dioxide, and the liquid allowed to stand for some time, an orange-yellow powder of **potassium monopermolybdate,** $K_2MoO_5.3H_2O$, is formed. It is almost insoluble in cold water, and the colloidal soln. is opalescent, but it becomes clear when the water is warmed. P. G. Melikoff and L. Pissarjewksy treated a cold soln. of this salt with a soln. of potassium hydroxide and hydrogen dioxide, and added alcohol to the red liquid. The pale brick-red precipitate of **potassium dipermolybdate,** $K_2MoO_6.H_2O$, or $K_2O_2.H_2O_2.MoO_3$, becomes yellow when exposed to air, and oxygen is given off. The compound explodes when triturated ; and gives off oxygen when treated with water. W. Muthmann and W. Nagel found the salt too unstable to analyze satisfactorily. The corresponding **sodium dipermolybdate** could not be obtained pure enough for analysis.

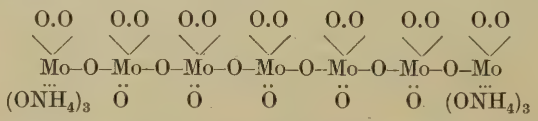
C. Bärwald suggested complex formulæ for the permolybdates which he prepared, but, according to W. Muthmann and W. Nagel, these formulæ are very unlikely. A. Mazzucchelli and G. Zangrilli studied complexes of the permolybdates and oxalates ; and A. Mazzucchelli and C. Ranucci, complexes with organic acids. A. Piccini, and P. Kasanezky obtained fluoroxypermolybdates as indicated below.

The permolybdates can be very roughly classed by means of the ratio R_2O : Mo =1 : 1 ; 1 : 2 ; 3 : 7 ; 1 : 3 ; 3 : 10 ; and 1 : 4. J. Möller reported anhydrous **ammonium permolybdate,** NH_4MoO_4, to be formed by the action of hydrogen dioxide on ammonium paramolybdate, and drying the product in vacuo. A. Fock gave for the axial ratios of the monoclinic prisms $a : b : c$=0·4693 : 1 : 0·2956, and β=112° 37·5′. E. Péchard said that by evaporating the soln. in vacuo, the *dihydrate* is formed in yellow monoclinic prisms which, according to H. Dufet, have the axial ratios $a : b : c$=1·4682 : 1 : 1·0259, and β=105° 45′. J. Möller found that the f.p. of aq. soln. of 0·6353, 1·0807, and 1·1406 grms. per 100 grms. of water are, respectively, —0·65°, —0·110°, and —0·113° ; whilst the electrical conductivities of aq. soln. of a mol of the salt in 15·65, 16·6, and 28·14 litres of water are, respectively, 67·88, 88·12, and 109·01. The data are taken to mean that the mol. wt. corresponds with the doubled formula $(NH_4)_2Mo_2O_8$. As indicated above, W. Muthmann and W. Nagel consider that both E. Péchard's, and J. Möller's analyses are wrong—*vide infra.* E. Péchard said that the salt swells up and decomposes when heated. It is sparingly soluble in water, but more soluble in alcohol. Alcohol extracts the salt from its aq. soln. J. Möller obtained anhydrous **potassium permolybdate,** $KMoO_4$, by the action of 20 per cent. hydrogen dioxide on powdered potassium trimolybdate which has been fused. The orange-coloured soln. deposits crystals of the salt in a few days. J. Möller preferred the doubled formula. E. Péchard reported the *dihydrate.* W. Muthmann and W. Nagel consider that the analyses of both J. Möller, and E. Péchard are wrong—*vide infra.* E. Péchard said that the crystals of the dihydrate are monoclinic prisms. The salt does not change its vol. when heated ; and it decomposes. It is sparingly soluble in cold water, and more soluble in hot water ; the aq. soln. is stable at ordinary temp., but, when boiled, it deposits potassium dimolybdate. It behaves like the ammonium salt towards alcohol. P. Blackman gave for the conductivity, μ, of $\frac{1}{2}K_2MoO_4$ in v litres of water at 25° :

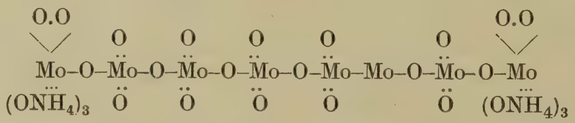
v . .	32	64	128	256	512	1024
μ . .	123	129	133	138	140	144

E. Péchard reported **sodium permolybdate,** $NaMoO_4.3H_2O$, to be formed by dissolving the dimolybdate in hydrogen dioxide and evaporating the soln. in vacuo. The yellow, prismatic crystals begin to melt in their water of crystallization, and near 200°, oxygen is given off. The salt is sparingly soluble in water, and insoluble in alcohol. E. Péchard prepared **copper permolybdate,** $Cu(MoO_4)_2.H_2O$, by double decomposition of the ammonium salt with a soln. of a cupric salt. The greenish-yellow powder is insoluble in water; soluble in aq. ammonia; and freely soluble in acids. The soln. in hydrochloric acid slowly evolves chlorine in the cold. It decomposes when heated. E. Péchard, and C. Bärwald similarly prepared **silver permolybdate,** $AgMoO_4$, in yellow, microscopic octahedra, which give off oxygen when heated. E. Péchard reported **barium permolybdate,** $Ba(MoO_4)_2.2H_2O$, to be formed from a soln. of barium dimolybdate in hydrogen dioxide, or by warming at 80° a soln. of ammonium permolybdate and barium chloride. The yellow, microscopic octahedra are decomposed when heated. C. Bärwald reported monoclinic prisms of the composition $8BaO.19MoO_3.2H_2O_2.13H_2O$ to be formed by the action of barium chloride soln. on $7(NH_4)_2O.18MoO_3.3H_2O_2.11H_2O$. The analysis is thus a close approximation to that of E. Péchard's salt. E. Péchard obtained **magnesium permolybdate,** $Mg(MoO_4)_2.10H_2O$, by a process like that used for the barium salt. The needle-like crystals melt at 70°, and decompose at about 200°. The salt is sparingly soluble in water, and less so in alcohol. E. Péchard prepared by double decomposition **mercurous permolybdate,** $HgMoO_4$, as an orange-yellow powder insoluble in a soln. of ammonium nitrate; and similarly also with **thallous permolybdate,** which is a yellow powder, insoluble in water, and which melts with the evolution of oxygen.

W. Muthmann and W. Nagel prepared **ammonium perparamolybdate,** $3(NH_4)_2O.7MoO_4.12H_2O$, by saturating a 20 per cent. soln. of hydrogen dioxide with ammonium paramolybdate, and evaporating the yellowish-red liquid. The orange-red, monoclinic crystals can be recrystallized from a soln. in a small proportion of water, but they are completely decomposed at 105°. The graphic formula for the orange-red salt is:



Another salt, $3(NH_4)_2O.5MoO_3.2MoO_4.6H_2O$, was prepared by W. Muthmann and W. Nagel by evaporating the mother-liquor. The salt decomposes at 170°. The formula for the lemon-yellow salt is:



It is probable that the salt prepared by C. Bärwald by the action of a dil. soln. of hydrogen dioxide on ammonium paramolybdate which he represented by $14NH_3.18MoO_3.3H_2O_2.18H_2O$, as well as that prepared by E. Péchard, as indicated above, and represented by the formula $NH_4MoO_4.2H_2O$, are impure forms of the perparamolybdate. In addition to the properties just indicated, C. Bärwald said that the sp. gr. of the crystals is 2·975, and that of the soln. sat. at 17·4° is 1·486. A. Mazzucchelli and C. Barbero found that the oxidation potential with a $2N$-soln. and platinum electrodes is 0·827 to 0·841 volt. W. Muthmann and W. Nagel obtained yellow, monoclinic crystals of **rubidium perparamolybdate,** $3Rb_2O.5MoO_3.2MoO_4.6H_2O$, from a soln. of rubidium paramolybdate in 5 per cent. hydrogen dioxide.

W. Muthmann and W. Nagel reported **potassium pertrimolybdate,** $K_2O.2MoO_3.MoO_4.3H_2O$, to be formed by evaporation over phosphorus pentoxide of a soln. of potassium trimolybdate in 20 per cent. hydrogen dioxide. A salt prepared in a similar manner by the action of dil. or conc., cold or hot hydrogen dioxide on potassium paramolybdate was represented by C. Bärwald by $6K_2O.16MoO_3.4H_2O_2.13H_2O$; and the salt, indicated above, prepared by E. Péchard, and represented by $KMoO_4.2H_2O$, was probably this compound. The yellow crystals have the properties indicated above. J. Möller found that soln. of 1·0144, 1·0892, and 1·6058 grms. of the salt in 100 grms. of water have the respective f.p. −0·086°, +0·101°, and −0·138°; and the electrical conductivities of soln. with 12·49, 18·32, and 19·67 mols $KMoO_4$ per litre are, respectively, 85·4, 90·5, and 92·1. W. Muthmann and W. Nagel prepared **rubidium pertrimolybdate,** $Rb_2O.2MoO_3.MoO_4.3H_2O$, from the mother-liquor of the 3 : 10-salt. The lemon-yellow, monoclinic crystals effloresce in air.

W. Muthmann and W. Nagel prepared **rubidium pertetramolybdate,** $Rb_2O.3MoO_3.MoO_4.4H_2O$, by allowing a dil. soln. of rubidium trimolybdate in 5 per cent. hydrogen dioxide to stand for some time. Pale, lemon-yellow crystals are formed. A hot soln. of cæsium tetramolybdate in 25 per cent. hydrogen dioxide gives orange-red, amorphous **cæsium pertetramolybdate,** $Cs_2O.4MoO_4.6H_2O$. When the soln. in hot water is rapidly cooled, it deposits the salt unchanged.

W. Muthmann and W. Nagel digested 10 grms. of anhydrous rubidium trimolybdate with 30 c.c. of warm, 25 per cent. hydrogen dioxide, and allowed the liquid to stand over sulphuric acid for 24 hrs. The resulting yellowish-red, amorphous mass of **rubidium perdecamolybdate,** $3Rb_2O.10MoO_4.14H_2O$, was washed with alcohol and ether. The evaporation of the mother-liquor obtained in the preparation of cæsium pertetramolybdate furnished yellow crystals of **cæsium perdecamolybdate,** $3Cs_2O.7MoO_3.3MoO_4.4H_2O$.

REFERENCES.

[1] P. Blackman, *Journ. Phys. Chem.*, **13**. 151, 1909; G. Werther, *Journ. prakt. Chem.*, (1), **84**. 198, 1861; *Arch. Sciences Genève*, (2), **11**. 82, 1861; L. Schönn, *Zeit. anal. Chem.*, **8**. 379, 1869; **9**. 41, 311, 1870; *Zeit. Chem.*, (2), **6**. 282, 1870; *Dingler's Journ.*, **210**. 317, 1873; G. Denigès, *Bull. Soc. Chim.*, (3), **3**. 797, 1890; (3), **5**. 293, 1891; (3), **6**. 22, 1891; *Compt. Rend.*, **110**. 1007, 1890; J. Bruhat and H. Dubois, *ib.*, **140**. 506, 1905; E. Péchard, *ib.*, **112**. 720, 1891; **114**. 1358, 1481, 1892; **115**. 227, 1892; *Ann. Chim. Phys.*, (6), **28**. 537, 1893; A. Piccini, *Zeit. anorg. Chem.*, **1**. 51, 1892; W. Muthmann and W. Nagel, *ib.*, **17**. 73, 1898; *Ber.*, **31**. 1836, 1898; A. Weller, *ib.*, **15**. 2592, 1882; P. G. Melikoff and L. Pissarjewsky, *ib.*, **31**. 632, 2448, 1898; *Zeit. anorg. Chem.*, **18**. 59, 1898; **19**. 414, 1899; L. Pissarjewsky, *ib.*, **24**. 108, 1900; *Zeit. phys. Chem.*, **40**. 368, 1902; *Journ. Russ. Phys. Chem. Soc.*, **32**. 155, 1900; **34**. 210, 1902; P. Kasanezky, *ib.*, **34**. 383, 1902; H. Dufet, *Bull. Soc. Min.*, **14**. 215, 1891; A. Fock, *Zeit. Kryst.*, **22**. 32, 1894; T. Fairley, *Journ. Chem. Soc.*, **31**. 141, 1877; L. Crismer, *Gaz. Med. Liege*, 77, 1888; *Bull. Soc. Chim.*, (3), **6**. 22, 1891; J. B. Cammerer, *Chem. Ztg.*, **15**. 957, 1891; J. Möller, *Zeit. phys. Chem.*, **12**. 555, 1893; J. Brode, *ib.*, **37**. 299, 1901; A. Mazzucchelli and M. Borghi, *Gazz. Chim. Ital.*, **40**. ii, 49, 241, 1910; A. Mazzucchelli and C. Barbero, *Atti Accad. Lincei*, (5), **15**. ii, 35, 109, 1906; A. Mazzucchelli, *ib.*, (5), **16**. i, 963, 1907; (5), **18**. ii, 259, 1909; A. Mazzucchelli and G. Zangrilli, *Gazz. Chim. Ital.*, **37**. ii, 326, 1907; **40**. ii, 65, 1910; A. Mazzucchelli and C. Ranucci, *ib.*, **43**. ii, 116, 426, 1914; R. Brandes, *Schweigger's Journ.*, **29**. 325, 331, 1820; A. C. Stark, *Pharm. Journ.*, (3), **23**. 757, 1893; G. C. Wittstein, *Repert. Pharm.*, **73**. 158, 1841; L. F. Svanberg and H. Struve, *Svenska Akad. Handl.*, **1**. 9, 1848; *Journ. prakt. Chem.*, (1), **44**. 257, 1848; *Phil. Mag.*, (3), **33**. 409, 524, 1848; C. Bärwald, *Beiträge zur Kenntnis Molybdäns*, Berlin, 1885; *Ber.*, **17**. 1206, 1884; F. Fichter and A. Goldoch, *Helvetica Chim. Acta*, **13**. 1200, 1930.

§ 17. Molybdenum Fluorides

J. J. Berzelius[1] obtained an aq. soln. of **molybdenum trifluoride** by dissolving hydrated molybdic oxide in hydrofluoric acid; the liquid forms a sticky, soluble, purple-red mass when evaporated, and when heated becomes brown and is then no longer soluble in water. Neither the anhydrous salt nor a hydrate has been obtained solid. A. Rosenheim and H. J. Braun added ammonium fluoride to a soln. of potassium molybdenum fluoride in hydrochloric acid, and obtained **ammonium molybdenum tetrafluoride,** $(NH_4)MoF_4.H_2O$, as a violet precipitate, which is more soluble than the potassium salt, and is hydrolyzed by water. If the violet soln. of this salt is allowed to stand over sulphuric acid, bluish-violet crystal plates of

ammonium molybdenum enneafluoride, $2MoF_3.3NH_4F$, or $(NH_4)_3Mo_2F_9$, are formed. This salt is readily hydrolyzed by water. J. J. Berzelius observed that a rose-red precipitate is formed when potassium fluoride is added to a soln. of molybdenum trifluoride. By electrolyzing soln. of molybdenum trioxide in conc. hydrofluoric acid, using a mercury cathode and adding the alkali fluorides to the soln., A. Rosenheim and T. H. Li prepared ammonium molybdenum enneafluoride, $(NH_4)_3Mo_2F_9.2H_2O$, as well as **potassium molybdenum enneafluoride,** $K_3Mo_2F_9.2H_2O$. A. Rosenheim and H. J. Braun obtained **potassium molybdenum tetrafluoride,** $KMoF_4.H_2O$, by the electro-reduction of a soln. of molybdenum trioxide in hydrochloric acid, and adding potassium fluoride to the liquor. The violet crystalline precipitate is gradually decomposed by water. It was not possible to prepare **sodium molybdenum tetrafluoride** pure enough to justify analysis.

J. J. Berzelius obtained a red soln. of **molybdenum tetrafluoride,** MoF_4, by the action of hydrofluoric acid on hydrated molybdenum dioxide. When slowly evaporated, the liquid becomes blue if the acid is not in excess, and it leaves a black crystalline residue which forms a red soln. with water. It is decomposed if more strongly heated. The blue molybdenum oxide gives a blue soln. with hydrofluoric acid, which does not crystallize. Complex salts have not been reported; although J. J. Berzelius observed that a precipitate is formed when potassium fluoride is added to the soln.

According to O. Ruff and F. Eisner,[2] they could not prepare **molybdenum pentafluoride,** MoF_5; but **molybdenum hexafluoride,** MoF_6, can be obtained by the action of hydrogen fluoride on molybdenum pentachloride, as well as from molybdenum pentachloride and antimony pentafluoride. It is best obtained by the action of fluorine on finely-divided molybdenum at 60° to 70°, and collecting the product in a glass receiver at −70°. It can be purified by redistillation. The white crystalline mass has a m.p. of 17°, and a b.p. of 35° at 760 mm. It is not affected by air. It is easily reduced to a blue fluoride; the presence of dust from the air is sufficient for this purpose. It forms a colourless soln. with an excess of water; moist air, or a little water, forms a blue molybdenum oxide. The salt does not react with chlorine; but with iodine it forms a brown product; it forms an orange product with sulphur; and it is indifferent towards sulphur dioxide. It reacts vigorously with gaseous ammonia, forming a brown powder. It is absorbed by aq. ammonia; with phosphorus it forms a pale blue substance, and it reacts with phosphorus trichloride and with phosphoryl chloride; it forms yellowish-brown crystals with arsenic trichloride; and it also reacts with antimony pentachloride. It is reduced by organic substances—like paraffin, blotting paper, animal skin, etc.—and becomes indigo-blue. Metals—copper, lead, iron, etc.—react forming coloured substances; but gold, and platinum have no action. It is absorbed by alkali-lye, and forms complex salts with alkali fluorides, but they have not been described. N. V. Sidgwick discussed the electronic structure of this salt.

REFERENCES.

[1] J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817; *Ann. Chim. Phys.*, (2), **17**. 5, 1921; *Pogg. Ann.*, **4**. 153, 1825; **6**. 331, 369, 1826; **7**. 261, 1826; H. J. Braun, *Untersuchungen über das Molybdän*, Berlin, 1904; A. Rosenheim and H. J. Braun, *Zeit. anorg. Chem.*, **46**. 311, 1905; A. Rosenheim and T. H. Li, *Ber.*, **56**. B, 2228, 1923.

[2] O. Ruff, *Zeit. angew. Chem.*, **20**. 1217, 1907; O. Ruff and F. Eisner, *Ber.*, **38**. 742, 1905; **40**. 2926, 1907; N. V. Sidgwick, *Journ. Chem. Soc.*, **125**. 2672, 1924.

§ 18. Molybdenum Oxyfluorides

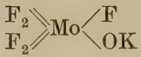
W. Wardlaw and R. L. Wormell[1] prepared a salt of tervalent molybdenum, namely, molybdenyl fluoride, $MoOF.3\frac{1}{2}H_2O$, or $MoOF.4H_2O$, by double decomposition of the oxychloride with ammonium fluoride in an air-free, aq. soln. The insoluble, buff-coloured precipitate has similar properties to the corresponding chloride and bromide, [$MoOR.4H_2O$]. The solubility, and ease of hydrolysis increase with increasing at. wt. of the halogen atom. The univalent molybdenyl radical, MoO, appears to persist in aq. soln. The oxygen atom seems to be firmly attached to the molybdenum nucleus and the whole behaves like a univalent metal. This conception is supported by the existence of other insoluble molybdenyl salts, such as the benzoate, phosphate, salicylate.

The salt of quinquevalent molybdenum, **molybdenum oxytrifluoride,** $MoOF_3$, has not been prepared. There is some doubt whether the **molybdenum trioxytetrafluoride,** $Mo_2O_3F_4$, of E. F. Smith and V. Oberholtzer contains quinquevalent or sexivalent molybdenum. It was obtained in red, needle-like crystals, by the action of hydrogen fluoride on molybdenum trioxide at 300° to 400°. It attacks glass; and gradually decomposes, forming blue oxide. It is deliquescent, and easily soluble in hydrofluoric acid, but not in water. Indications of other products were obtained.

Although molybdenum oxytrifluoride is unknown, a number of complex salts has been prepared. These are of two types: $5RF.3MoOF_3$, and $2RF.MoOF_3$. F. Mauro found that a soln. of ammonium molybdenum oxypentafluoride in hot hydrofluoric acid, when concentrated and cooled, furnishes sky-blue needles of **ammonium molybdenum trioxytetradecafluoride,** $5NH_4F.3MoOF_3.H_2O$, which, under the microscope, appear as hexagonal crystals. The salt is decomposed by water, and acts as a reducing agent. The crystals are isomorphous with the corresponding sexivalent salt, $5NH_4F.3MoO_2F_2.H_2O$. The analogous **potassium molybdenum trioxytetradecafluoride,** $5KF.3MoOF_3.H_2O$, was prepared in a similar manner.

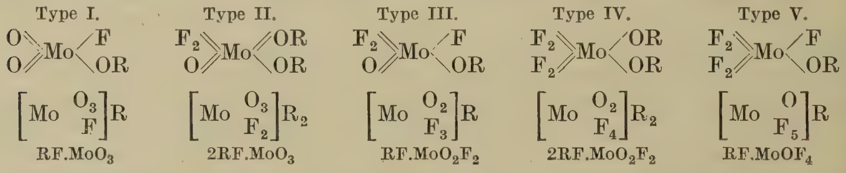
F. Mauro and R. R. Panebianco dissolved molybdenum dioxide in hydrofluoric acid and added ammonia until the soln. became brownish-red; hydrofluoric acid was then added until the soln. became green. The liquid was then evaporated when sky-blue plates of **ammonium oxypentafluomolybdate,** $2NH_4F.MoOF_3$, or $(NH_4)_2[MoOF_5]$, were formed. A soln. of this salt was also obtained by the electrolysis of $2NH_4F.MoO_2F_2$. E. Scacchi gave for the axial ratios of the rhombic bipyramids $a:b:c=0·4214:1:1·0260$. The crystals are isomorphous with those of $2NH_4F.MoO_2F_2$. L. P. Liechti and B. Kempe observed that the addition of molybdenum pentachloride to a soln. of potassium fluoride gives a precipitate presumably **potassium oxypentafluomolybdate,** $2KF.MoOF_3.H_2O$, a salt obtained by F. Mauro by adding potassium fluoride to a soln. of hydrated molybdenum dioxide in hydrofluoric acid; and also by the electrolysis of a soln. of $2KCl.MoO_2F_2$. E. Scacchi gave for the axial ratios of the monoclinic prisms, $a:b:c=0·9997:1:1·0320$, and $\beta=99° 4'$. The (010)-cleavage is indistinct. F. Mauro added that the salt changes very little on exposure to air, and when heated, it gives off water, etc., forming normal potassium molybdate. The salt is decomposed by water or dil. hydrochloric acid, but not by dil. hydrofluoric acid. It reduces soln. of salts of copper, silver, and gold. F. Mauro also prepared **copper molybdenum pentafluomolybdate,** $CuF_2.MoOF_3.4H_2O$, in blue, six-sided monoclinic plates which, according to E. Scacchi, have the axial ratios $a:b:c=1·4745:1:1·0929$, and $\beta=85° 43'$, and are isomorphous with $CuF_2.MoO_2F_2.4H_2O$. The salt can be crystallized unchanged from hydrofluoric acid; but it is decomposed by water. Likewise also with **zinc molybdenum oxypentafluomolybdate,** $ZnF_2.MoOF_3.6H_2O$, which furnishes blue, deliquescent trigonal crystals isomorphous with $ZnF_2.MoO_2F_2.6H_2O$, and with the axial ratio $a:c=1:0·5136$. F. Mauro also prepared **thallous molybdenum oxypentafluomolybdate,** $2TlF.MoOF_3$, in dark green rhombic bipyramids with the axial ratios $a:b:c=0·4329:1:1·0295$. The salt begins to decompose at 240°.

O. Ruff and F. Eisner[2] said that **molybdenum oxytetrafluoride,** $MoOF_4$, is formed in the action of fluorine on a molybdenum oxide; and they prepared it by distilling hydrogen fluoride into a well-cooled vessel containing molybdenum oxytetrafluoride; the product is warmed to 30°, and, when the reaction is ended, it is distilled from a sulphuric acid bath at 230°. The white, hygroscopic solid becomes blue when exposed to air, and deliquesces. Its sp. gr. is 3·001 at 20°; it sinters at 96°; melts at 97° to 98° and boils at about 180°. It dissolves with a hissing noise in water, and forms a colourless soln.; and similarly with alcohol. When the aq. soln. is evaporated, molybdenum trioxide remains. The salt dissolves with the evolution of a gas in chloroform and ether, forming green or yellow soln.; it is sparingly soluble in benzene, and carbon disulphide; and insoluble in toluene. It is reduced by soln. of organic substances. With sulphuric acid it forms a colourless soln. giving off hydrogen fluoride; and it gives brown soln. with phosphorus trichloride, phosphoryl chloride, arsenic trichloride, sulphur monochloride, and pyridine. G. Marchetti observed that when potassium molybdate, or potassium dioxytetrafluomolybdate is treated with conc. hydrofluoric acid, it furnishes **potassium oxypentafluomolybdate,** $KF.MoOF_4$, or $K[MoOF_5]$, or



$$\begin{matrix}F_2\\F_2\end{matrix}\!>\!\mathrm{Mo}\!<\!\begin{matrix}F\\OK\end{matrix}$$

J. J. Berzelius[3] found that molybdenum trioxide dissolves freely in hydrofluoric acid, forming a colourless soln. which has a sour, and metallic taste; the liquid shows no signs of crystallization when it is evaporated, and it acquires a green or blue tinge owing to reduction by particles of organic dust. The dried mass is only partially soluble in water; the insoluble portion consists of molybdenum trioxide mixed with a little fluoride. H. O. Schulze observed that molybdic acid reacts with metal fluorides, forming **molybdenum dioxydifluoride,** MoO_2F_2; whilst O. Ruff and F. Eisner obtained it by the action of hydrogen fluoride on molybdenum dioxydichloride as in the case of the preparation of the oxytetrafluoride (*q.v.*). The white crystalline sublimate has a faint blue tinge; it has a sp. gr. 3·494 at 19°; it begins to sublime at 265°, and at 271° sublimation rapidly occurs. It is very hygroscopic, and in moist air it forms hydrofluoric and molybdic acids. It forms a colourless soln. with water; if only a small proportion of water is used, the soln. is blue. It is also soluble in methyl and ethyl alcohols; sparingly soluble in chloroform, carbon tetrachloride, and ether; and insoluble in toluene. The hot soln. in pyridine deposits on cooling a white, microcrystalline substance. It is soluble in sulphuryl chloride, phosphorus and arsenic trichlorides; and in silicon tetrachloride—when these soln. are warmed, a gas is developed. A number of **oxyfluomolybdates** has been prepared. Starting from the normal molybdate, $(RO)_2MoO_2$, there are:



Type I.	Type II.	Type III.	Type IV.	Type V.
$\begin{matrix}O\\O\end{matrix}\!>\!\mathrm{Mo}\!<\!\begin{matrix}F\\OR\end{matrix}$	$\begin{matrix}F_2\\O\end{matrix}\!>\!\mathrm{Mo}\!<\!\begin{matrix}OR\\OR\end{matrix}$	$\begin{matrix}F_2\\O\end{matrix}\!>\!\mathrm{Mo}\!<\!\begin{matrix}F\\OR\end{matrix}$	$\begin{matrix}F_2\\F_2\end{matrix}\!>\!\mathrm{Mo}\!<\!\begin{matrix}OR\\OR\end{matrix}$	$\begin{matrix}F_2\\F_2\end{matrix}\!>\!\mathrm{Mo}\!<\!\begin{matrix}F\\OR\end{matrix}$
$\left[\mathrm{Mo}\begin{matrix}O_3\\F\end{matrix}\right]R$	$\left[\mathrm{Mo}\begin{matrix}O_3\\F_2\end{matrix}\right]R_2$	$\left[\mathrm{Mo}\begin{matrix}O_2\\F_3\end{matrix}\right]R$	$\left[\mathrm{Mo}\begin{matrix}O_2\\F_4\end{matrix}\right]R_2$	$\left[\mathrm{Mo}\begin{matrix}O\\F_5\end{matrix}\right]R$
$RF.MoO_3$	$2RF.MoO_3$	$RF.MoO_2F_2$	$2RF.MoO_2F_2$	$RF.MoOF_4$

Representatives of Type I have not been obtained; and Type V has been discussed above. Type II is represented by **ammonium trioxydifluomolybdate,** $NH_4[MoO_3F_2]$, or $2NH_4F.MoO_3$, which F. Mauro[4] obtained by mixing a soln. of the dioxypentafluomolybdate with ammonia. The precipitate is dissolved in a hot ammoniacal soln. of ammonium fluoride, and the soln. evaporated spontaneously in air or over sulphuric acid. The rhombic bipyramids were found by A. Scacchi to have the axial ratios $a:b:c=0·5746:1:0·6771$; and to exhibit twinning and trilling. U. Alvisi found that the salt is insoluble in water, and, added F. Mauro, water decomposes the salt. It is not changed at 100°, but at a higher temp. decomposition sets in. F. Mauro prepared **thallous dioxytrifluomolybdate,** $Tl[MoO_2F_3]$, or $TlF.MoO_2F_2$, from a soln. of the dioxytetrafluomolybdate in conc. hydrofluoric acid. The salt begins to decompose at 240°. A. Scacchi found that the monoclinic prisms have the axial ratios $a:b:c=0·6199:1:1·3976$, and $\beta=93° 53'$, and are isomorphous with the ammonium salt.

Type III is represented by **ammonium dioxytrifluoride,** $NH_4[MoO_2F_3]$, or $NH_4F.MoO_2F_2$, prepared by F. Mauro by evaporating over sulphuric acid a hydrofluoric acid soln. of the hexoxyhenafluomolybdate, and U. Alvisi, by the action of hydrofluoric acid on 1 : 24-phosphomolybdic acid or its ammonium salt. The colourless, monoclinic prisms were found by A. Scacchi to have the axial ratios $a:b:c=0\cdot6302:1:0\cdot4255$, and $\beta=94° 7'$, and to be isomorphous with the thallium salt. The salt turns green on exposure to air. M. Delafontaine described a *hydrate,* $NH_4F.MoO_2.H_2O$, obtained in rhombic crystals by the action of hydrofluoric acid on dioxytetrafluomolybdate, or an acid ammonium molybdate. The form of the crystals is the same as that of the dioxypentafluomolybdate, and M. Delafontaine's determination of the contained molybdenum applies to either salt, hence F. Mauro believed that M. Delafontaine's hydrate is really the dioxypentafluomolybdate. M. Delafontaine also reported prismatic crystals of **potassium dioxytrifluomolybdate,** $K[MoO_2F_3].H_2O$, or $KF.MoO_2F_2.H_2O$, to be formed by the action of hydrofluoric acid on an acid potassium molybdate, or the dioxytetrafluomolybdate. G. Marchetti could not prepare this salt, and he regarded the product as a mixture of the dioxytetrafluomolybdate with another salt as well as $KF.MoOF_4$. There are similar doubts about M. Delafontaine's **rubidium dioxytrifluomolybdate,** $RbF.MoO_2F_2.H_2O$.

Type IV is represented by **ammonium dioxytetrafluomolybdate,** $2NH_4F.MoO_2F_2$, or $(NH_4)_2[MoO_2F_4]$, prepared by F. Mauro by evaporating a soln. of ammonium trioxydifluomolybdate, and U. Alvisi obtained it from the mother-liquid obtained in the preparation of this salt. The colourless plates or prisms are isomorphous with the corresponding oxyfluocolumbate and oxyfluotungstate. The rhombic bipyramids were found by A. Scacchi to have the axial ratios $a:b:c=0\cdot4207:1:0\cdot0164$. F. Mauro found that the salt is unchanged at 100°, but is decomposed at a higher temp. It is freely soluble in water, and the evaporation of the aq. soln. gives the salt unchanged. M. Delafontaine reported that the monohydrate is produced by evaporating a soln. of ammonium paramolybdate in hydrofluoric acid and ammonium fluoride. The crystals are said to be triclinic like the analogous potassium salt with which they are isomorphous. It is rather more soluble than the potassium salt. By evaporating a soln. of ammonium dioxytetrafluomolybdate or trioxydifluomolybdate in ammonia over sulphuric acid or in air, F. Mauro obtained octahedral crystals of **ammonium trioxytrifluomolybdate,** $(NH_4)_2O.NH_4F.MoO_2F_2$, or $MoO_3.3NH_4F$, or $F_3Mo(ONH_4)_3$, or $(NH_4)_3[MoO_3F_3]$; these crystals are isomorphous with the corresponding tungstate. They are stable at 100°, and when roasted furnish molybdenum trioxide. The salt can be crystallized unchanged from its aq. soln. L. Pauling found that there are four molecules per unit face-centred, cubic lattice. The space-lattice has $a=9\cdot10$ A., and the interatomic distances Mo to $F=1\cdot9$ A., and F to F, 5·3 A. The octahedral cleavage is perfect.

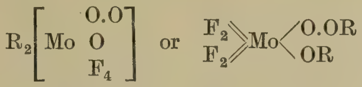
M. Delafontaine prepared **sodium dioxytetrafluomolybdate,** $Na_2[MoO_2F_4].\frac{1}{2}H_2O$, or $2NaF.MoO_2F_2.\frac{1}{2}H_2O$, from a soln. of normal sodium molybdate in a small excess of hydrofluoric acid. The crystals lose their water when heated in a closed vessel; and are decomposed when heated in air forming normal sodium molybdate. J. J. Berzelius mixed potassium fluoride with a soln. of molybdenum trioxide in hot hydrofluoric acid, and obtained a precipitate of what was probably **potassium dioxytetramolybdate,** $K_2[MoO_2F_4].H_2O$, or $2KF.MoO_2F_2.H_2O$; G. Marchetti added the theoretical proportion of potassium hydroxide instead of the fluoride; J. J. Berzelius, and M. Delafontaine obtained the salt from a soln. of normal potassium molybdate in a small excess of hydrofluoric acid; and U. Alvisi, from a soln. of potassium hydrofluoride and 1 : 24-phosphomolybdic acid. The tabular or scaly crystals were said by J. J. Berzelius to resemble the crystals of boric acid, and those of the corresponding tungsten salt; M. Delafontaine also noted their resemblance to those of the oxyfluo-columbates, titanates, and tungstates; the crystals were said to be triclinic, but A. Scacchi showed that they are monoclinic prisms with the axial ratios $a:b:c=1\cdot0006:1:0\cdot9994$, and $\beta=103° 29'$. G. Marchetti said that the anhydrous salt is obtained by heating the hydrate to 100° ; or by crystallization from a soln. in hot hydrofluoric acid. M. Delafontaine, and J. J. Berzelius said that the crystals are stable in air ; and they lose about 6 per cent. of water at about 60° ; and they melt without further decomposition when heated, forming a yellowish-brown mass. When roasted in air, normal potassium molybdate is formed. Hydrofluoric acid is given off when the salt is heated with conc. sulphuric acid. The salt dissolves freely in boiling water, and the cooling soln. deposits the unchanged crystals.

F. Mauro prepared **copper dioxytetrafluomolybdate,** $CuF_2.MoO_2F_2.4H_2O$, or $Cu[MoO_2F_4].4H_2O$, by evaporating a hydrofluoric acid soln. of a mol each of copper oxide and molybdenum trioxide. The pale blue monoclinic plates were found by A. Scacchi to have the axial ratios $a:b:c=1·4828:1:1·0987$, and $\beta=85° 9'$, and to be isomorphous with the corresponding copper oxyfluotungstate and columbate, as well as with the copper fluosilicate, titanate and stannate. F. Mauro said the salt is stable in dry air ; in moist air, water is absorbed ; at 115°, it loses its water and becomes pale green ; and at 130°, the evolution of hydrofluoric acid begins. M. Delafontaine prepared **zinc dioxytetrafluomolybdate,** $Zn[MoO_2F_4].6H_2O$, or $ZnF_2.MoO_2F_2.6H_2O$, by evaporating a hydrofluoric acid soln. of eq. proportions of zinc oxide and molybdenum trioxide. The trigonal prisms have the axial ratio $a:c=1:0·5166$, and the salt is isomorphous with the oxypentafluomolybdate and columbates of magnesium, zinc, cadmium, manganese, cobalt, and nickel, and with the corresponding fluosilicates, fluotitanates, and fluostannates. H. Grimm studied the miscibility of these crystals with those of zinc fluostannate. B. Gossner gave 2·151 for the sp. gr. When roasted, normal zinc molybdate is formed. M. Delafontaine also prepared **cadmium dioxytetrafluomolybdate,** $Cd[MoO_2F_4].6H_2O$, or $CdF_2.MoO_2F_2.6H_2O$, as in the case of the zinc salt. The trigonal prisms have the axial ratio $a:c=1:0·5159$. M. Delafontaine prepared **thallous dioxytetrafluomolybdate,** $Tl_2[MoO_2F_4]$, or $2TlF.MoO_2F_2$, by the double decomposition of thallous sulphate and potassium dioxytetrafluomolybdate, or from a hydrofluoric acid soln. of normal thallous molybdate, or eq. proportions of thallous oxide and molybdenum trioxide. M. Delafontaine said that it is monohydrated, and F. Mauro that it is anhydrous. It does not lose in weight at 200° ; but when roasted in air, it forms normal thallous molybdate. A. Scacchi found that the rhombic bipyramids have the axial ratios $a:b:c=0·4276:1:1·0247$. M. Delafontaine prepared dark red, hexagonal crystals of **cobalt dioxytetrafluomolybdate,** $Co[MoO_2F_4].6H_2O$, or $CoF_2.MoO_2F_2.6H_2O$, which are stable in dry air ; and **nickel dioxytetrafluomolybdate,** $Ni[MoO_2F_4].6H_2O$, or $NiF_2.MoO_2F_2.6H_2O$.

F. Mauro reported **ammonium hexoxyhenafluomolybdate,** $5NH_4F.3MoO_2F_2.H_2O$, to be formed by the evaporation of the hydrofluoric acid soln. of ammonium dioxytetrafluo- or trioxydifluo-molybdate. The colourless, six-sided, hexagonal prisms soon become opaque in air ; they lose part of their water at 100°, and at a higher temp., they decompose. The aq. soln. has an acidic reaction ; and gives off hydrofluoric acid when heated. F. Mauro also prepared **ammonium dioxypentafluomolybdate,** $3NH_4F.MoO_2F_2$, or $(NH_4)_3Mo.O_2F_5$, by evaporating soln. of ammonium paramolybdate in an excess of hydrofluoric acid and ammonium fluoride. The colourless, rhombic prisms were found by A. Scacchi to have the axial ratios $a:b:c=0·5452:1:0·8767$. F. Mauro observed that the salt decomposes when heated ; it dissolves in water with an acidic reaction ; and A. Miolatti and U. Alvisi showed that the electrical conductivity of the aq. soln. indicates that the salt is hydrolyzed. The eq. conductivity, λ, of a soln. with $(3NH_4F.MoO_2F_2)$ in v litres :

v . .	32	64	128	256
λ . .	107·5	117·9	133·4	143·2

There is a series of salts—the **oxyfluopermolybdates**—which is related to the oxyfluomolybdates much as the permolybdates are related to the molybdates. They were prepared by A. Piccini[5] by the action of hydrogen dioxide on the oxyfluomolybdates. They can be regarded as oxyfluomolybdates in which an oxygen atom is replaced by a bivalent C·O-group:



$$R_2\left[Mo\begin{matrix}O.O\\O\\F_4\end{matrix}\right]$$

The yellow salts crystallize well, and are stable. Their aq. soln. give the typical reaction of hydrogen dioxide. A. Piccini prepared **ammonium trioxypentafluomolybdate,** $3NH_4F.MoO_3F_2$, or $(NH_4)_3[MoF_5O(O_2)]$, by evaporating a soln. of ammonium paramolybdate and fluoride in hydrogen dioxide and hydrofluoric acid; or by treating ammonium dioxypentafluoride with hydrogen dioxide. The yellow prisms or plates become opaque in air; they are not changed at 100°; they are very soluble in water; and in platinum vessels, the aq. soln. decomposes with the evolution of oxygen.

A. Piccini prepared **potassium trioxytetrafluopermolybdate,** $F_4Mo(OOK)(OK).H_2O$, or $K_2[F_4MoO(O_2)].H_2O$, by cooling a warm 4 per cent. soln. of hydrogen dioxide soln. of the dioxytetrafluomolybdate, and recrystallizing the product from dil. hydrogen dioxide. The yellow, monoclinic plates have the axial ratios $a : b : c = 0{\cdot}9958 : 1 : 0{\cdot}9780$, and $\beta = 102° 13'$. The crystals are isomorphous with those of the rubidium salt, with the corresponding tungstate, as well as with those of the dioxytetrafluomolybdate and oxypentafluomolybdate. The (010)-cleavage is incomplete. The salt is stable in air; it loses some water at 100°; and at 150°, it gives off oxygen; and at a higher temp., it forms normal potassium molybdate. It gives off no fluorine if dry in vacuo. It is sparingly soluble in cold water, and freely soluble in hot water; and it separates unchanged from its aq. soln., and its soln. in hydrofluoric acid. According to A. Mazzucchelli and C. Barbero, a mol of the salt in 15 litres of water has an oxidation potential 0·881 to 0·933 volt with platinum electrodes; and after the addition of an equal vol. of a soln. of potassium dioxytetrafluomolybdate of the same concentration, the oxidation potential is 0·872 to 0·920 volt. If a mol of this salt be treated with 4 mols of hydrogen dioxide, P. Kasanetzky found that microscopic, rhombic crystals of **potassium pentoxydifluopermolybdate,** $K_2[F_2MoO_3(O_2)].H_2O$, are formed. With the continued action of hydrogen dioxide, all the fluorine is displaced, and potassium permolybdate is formed. A. Piccini prepared **rubidium trioxytetrafluopermolybdate,** $Rb_2[F_4MoO(O_2)].H_2O$, or $F_4Mo(ORb)(OORb).H_2O$, by mixing a soln. of rubidium chloride in hydrogen dioxide with a soln. of molybdenum trioxide in hydrofluoric acid, and recrystallizing the product from a soln. of hydrogen dioxide. The yellow, monoclinic plates have the axial ratios $a : b : c = 1{\cdot}0260 : 1 : 0{\cdot}9938$, and $\beta = 102° 15'$. This salt is isomorphous with the corresponding potassium salt; but is more easily soluble, otherwise, it behaves like the potassium salt. A. Piccini also prepared **cæsium trioxytetrafluopermolybdate,** $Cs_2[F_4MoO(O_2)].H_2O$, or $F_4Mo(OCs)(OOCs).H_2O$, as in the case of the rubidium salt with which it is quite similar.

REFERENCES.

[1] E. F. Smith and V. Oberholtzer, *Zeit. anorg. Chem.*, **4**. 236, 1893; F. Mauro, *ib.*, **2**. 25, 1892; *Gazz. Chim. Ital.*, **18**. 120, 1888; **19**. 179, 1889; **20**. 109, 1890; *Atti Accad. Lincei*, (4), **4**. 481, 1888; (4), **5**. 398, 1889; (5), **2**. ii, 282, 1893; F. Mauro and R. R. Panebianco, *ib.*, (3), **6**. 205, 1882; *Gazz. Chim. Ital.*, **12**. 180, 1882; E. Scacchi, *ib.*, (4), **4**. 489, 1887; L. P. Liechti and B. Kempe, *Liebig's Ann.*, **170**. 344, 1864; W. Wardlaw and R. L. Wormell, *Journ. Chem., Soc.*, 1087, 1927.

[2] O. Ruff and F. Eisner, *Ber.*, **38**. 742, 1905; **40**. 2926, 1907; O. Ruff, *Zeit. angew. Chem.*, **20**. 1217, 1907.

[3] J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817; *Ann. Chim. Phys.*, (2), **17**. 5, 1921; *Pogg. Ann.*, **4**. 153, 1825; **6**. 331, 369, 1826; **7**. 261, 1826; H. O. Schulze, *Journ. prakt. Chem.*, (2), **21**. 442, 1880; O. Ruff and F. Eisner, *Ber.*, **38**. 742, 1905; **40**. 2926, 1907; O. Ruff, *Zeit. angew. Chem.*, **20**. 1217, 1907; G. Marchetti, *Zeit. anorg. Chem.*, **10**. 66, 1895.

[4] F. Mauro, *Zeit. anorg. Chem.*, **2**. 25, 1892; *Gazz. Chim. Ital.*, **18**. 120, 1888; *Atti Accad. Lincei*, (4), **4**. 481, 1888; (4), **5**. 398, 1889; (5), **2**. ii, 282, 1893; A. Scacchi, *ib.*, (4), **4**. 489, 1887;

J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817 ; *Ann. Chim. Phys.*, (2), **17**. 5, 1921 ; *Pogg. Ann.*, **4**. 153, 1825 ; **6**. 331, 369, 1826 ; **7**. 261, 1826 ; M. Delafontaine, *Journ. prakt. Chem.*, (1), **95**. 136, 1865 ; *Liebig's Ann.*, **127**. 293, 1886 ; *Arch. Sciences Geneve*, (2), **23**. 5, 1865 ; (2), **30**. 232, 1867 ; U. Alvisi, *Atti Accad. Lincei*, (5), **3**. 494, 1894 ; *Gazz. Chim. Ital.*, **24**. i, 523, 1894 ; A. Miolatti and U. Alvisi, *Atti Accad. Lincei*, (5), **6**. 376, 1897 ; G. Marchetti, *Zeit. anorg. Chem.*, **10**. 66, 1895 ; A. Piccini, *ib.*, **1**. 51, 1892 ; B. Gossner, *Zeit. Kryst.*, **42**. 481, 1906 ; H. Grimm, *Zeit. Elektrochem.*, **30**. 467, 1924 ; L. Pauling, *Journ. Amer. Chem. Soc.*, **46**. 2738, 1924.

[5] A. Piccini, *Zeit. anorg. Chem.*, **1**. 51, 1892 ; A. Mazzucchelli and C. Barbero, *Atti Accad. Lincei*, (5), **15**. ii, 35, 109, 1906 ; P. Kasanetzky, *Journ. Russ. Phys. Chem. Soc.*, **34**. 383, 1902.

§ 19. Molybdenum Chlorides

Five chlorides of molybdenum have been reported in which the molybdenum is bi-, ter-, quadri-, quinque-, and sexivalent. L. F. Svanberg and H. Struve,[1] and C. J. Keyser prepared **molybdous chloride,** or **molybdenum dichloride,** $MoCl_2$, containing bivalent molybdenum. The compound was investigated by C. W. Blomstrand, and A. Atterberg. The analyses by C. W. Blomstrand, and by L. P. Liechti and B. Kempe agree with the empirical formula $MoCl_2$, but the mol. wt. calculated from its effect on the b.p. of alcohol was found by W. Muthmann and W. Nagel to agree with the formula $(MoCl_2)_3$, or Mo_3Cl_6. C. W. Blomstrand also interpreted the chemical behaviour to agree best with the assumption that the bivalent molybdenum forms the polymerized chloride, Mo_3Cl_6. He prepared it by heating the trichloride in a current of dry carbon dioxide, and L. P. Liechti and B. Kempe, and W. Muthmann and W. Nagel showed that it is necessary to exclude air and moisture, and to regulate the temp. carefully. C. W. Blomstrand also prepared the dichloride by heating a mixture of molybdenum and mercurous chloride—a large proportion of trichloride is formed at the same time ; by passing chlorine, largely diluted with carbon dioxide over the moderately-heated metal ; and as a by-product in the preparation of molybdenum pentachloride. According to K. Lindner and co-workers, the best method of preparation is to pass carbonyl chloride vapour over the powdered metal heated between 600° and 620°. The result at 400° is to form some trichloride which does not volatilize ; at 490°, the boat contains some trichloride, and a little trichloride sublimes ; at 520°, the boat contains both di- and trichlorides, and some of the latter sublimes ; at 590°, the boat contains the dichloride, and the tri- and pentachlorides sublime ; at 610° and 620°, the boat contains the dichloride, and the sublimate a little pentachloride ; at 670°, the boat contains some dichloride, and molybdenum pentachloride sublimes ; and between 700° and 1000°, there is a sublimate of the pentachloride. The heavy yellow layer of the dichloride which forms on the molybdenum protects the metal from attack by the carbonyl chloride. The dichloride is then extracted with conc. hydrochloric acid and the residual metal is again treated with carbonyl chloride. The compound, $HMo_3Cl_7.4H_2O$, separates almost quantitatively from the acid soln. in the form of long, yellow needles. Less favourable but useful results are obtained by the reduction of molybdenum pentachloride with finely-divided aluminium in the presence of ignited quartz powder (to moderate the violence of the reaction). The product is subsequently extracted with hydrochloric acid. The yield is considerably diminished by the reduction of molybdenum pentachloride to other chlorides. The dichloride prepared by C. W. Blomstrand was amorphous, and matte ; and, according to L. P. Liechti and B. Kempe, after treatment with nitric acid, it is yellow. C. J. Keyser, and C. W. Blomstrand said that it is stable in air, and very difficult to volatilize. W. Biltz and C. Fendius gave 3·714 for the sp. gr. at 25°/4°, and 44·9 for the mol. vol. L. P. Liechti and B. Kempe found that when heated in air, it gives a sublimate of molybdenum trioxide and a black residue, which, on continued roasting, also volatilizes as molybdenum trioxide. When heated in hydrogen, the dichloride is reduced to the metal. C. J. Keyser, and C. W. Blomstrand said that the dichloride is insoluble in water ; but it dissolves easily and completely in hydrochloric, and the other halogen acids ; it is also soluble in sulphuric acid. L. P. Liechti and B. Kempe found that aq. ammonia dissolves the dichloride, and then transforms it into a brown, nitrogenous powder. The dichloride dissolves in alcohol, and ether without undergoing chemical action. K. Lindner and co-workers observed that when a sat. alcoholic soln. of the dichloride is mixed with twice its vol. of ether, ice-cold, and treated with ammonia gas, a pale yellow, voluminous precipitate of **molybdenous diamminochloride,** $Mo_3Cl_6(NH_3)_2.2C_6H_5OH$, is formed. It decomposes at 100°. When molybdenous dichloride is dissolved in ether containing 5 per cent. of ethyl alcohol, and the soln. evaporated in vacuo, the compound $Mo_3Cl_6.C_2H_5OH$ remains as light yellow powder stable in air; the alcohol cannot be removed by heating in an inert atmosphere without decomposition. Addition of alcoholic silver nitrate to the alcoholic soln. precipitates silver chloride; the mother-liquor deposits the compound $Mo_3Cl_4(NO_3)_2.EtOH$ on keeping, but on immediate treatment of the filtrate with ether, the nitrate, $Mo_3Cl_4(NO_3)_2$, is obtained. W. Hampe found that an ethereal soln. of the dichloride does not conduct the electric current; the alcoholic soln. conducts a little, probably in consequence of the formation of a little hydrochloric acid. Hydrogen is liberated from the cathode, and a black oxide is gradually deposited. W. Muthmann and W. Nagel added that the electrolysis of a soln. in 96 per cent. alcohol furnishes hydrogen and molybdenum tetrachlorodihydroxide at the cathode, and at the anode, aldehyde and ethyl chloride. C. W. Blomstrand, and K. Wolf found that a soln. of potassium or sodium hydroxide dissolves the dichloride forming a yellow soln.; and with boiling alkali-lye, molybdenum dihydroxide, $Mo(OH)_2$, is formed. The yellow soln. in alkali-lye slowly absorbs carbon dioxide from the air, and when carbon dioxide is passed through the soln., or acetic acid is added, molybdenum tetrachlorodihydroxide is formed.

C. W. Blomstrand, and A. Atterberg supposed that molybdous chloride contained the group Mo_3Cl_4. This is evidenced by the products obtained by C. W. Blomstrand by the action of strong acids on molybdous chloride, namely $(Mo_3Cl_4)X_2$, where X represents Cl, Br, or I, associated with ammonium or potassium halide; and by the various mixed salts obtained by C. W. Blomstrand, and A. Atterberg, namely, $Mo_3Br_4X_2.nH_2O$, where X_2 denotes F_2, Cl_2, Br_2, I_2, MoO_4, SO_4, CrO_4, $(H_2PO_4)_2$, and C_2O_4. According to I. Koppel, the bivalency of the contained molybdenum is illustrated by the development of hydrogen when the bromide $Mo_3Br_4(OH)_2$ is treated with alkali-lye; and by the precipitation of silver from an ammoniacal silver soln. when treated with $(Mo_3Cl_4)HCl.4H_2O$. The effect of the salt on the b.p. of alcohol agrees with the formula $(MoCl_2)_3$. The electrical conductivity of soln. of all the soluble derivatives is explained by assuming that the Mo_3Cl_4 is usually the cation, and hydrolysis proceeds as far as the Mo_3Cl_4-group. The dehydration phenomenon supports the same hypothesis. The radicle Mo_3Cl_4 is amphoteric acting either as a basic or as an acidic radicle. I. Koppel also emphasized the great stability of the Mo_3Cl_4-radicle; and the resistance it offers to oxidation. These results are in accord with some hypothesis analogous to A. Werner's co-ordination theory. This subject was discussed by K. Lindner, and W. Biltz.

C. W. Blomstrand said that a *trihydrate*, $Mo_3Cl_6.3H_2O$, is deposed in pale, yellow, insoluble scales from a soln. of the anhydrous chloride in moderately dilute hydrochloric acid. If a soln. in hot hydrochloric acid be evaporated on a water-bath, pale yellow needles or prisms are formed; these are soluble in water, alcohol, and ether. The compound was regarded by C. W. Blomstrand as a *hexahydrate*, $Mo_3Cl_6.6H_2O$; by L. P. Liechti and B. Kempe, as a *hemienneahydrate*, $Mo_3Cl_6.4\frac{1}{2}H_2O$; and by A. Rosenheim and F. Kohn, as $Mo_3Cl_3.HCl.4H_2O$. The last hypothesis is confirmed by the fact that when exposed to air, the crystals lose hydrogen chloride and become green, but the yellow colour is restored in an atmosphere of hydrogen chloride. The reaction with an ammoniacal soln. of silver is in agreement with the bivalency of the contained molybdenum. When this compound is heated at 100° or 130° in an atm. of hydrogen chloride, a yellow residue of the *monohydrate*, $Mo_3Cl_6.H_2O$, is formed. The compound $Mo_3Cl_6.HCl.4H_2O$ behaves as if it were **chloroaquomolybdous acid,** $H[Mo_3Cl_7(H_2O].3H_2O$. Water removes only one atom of chlorine, but when a soln. in potash-lye is treated with acetic acid, **molybdous diaquotetrachlorodihydroxide,** $Mo_3Cl_4(OH)_2.8H_2O$, or $[Mo_3Cl_4(H_2O_2)](OH)_2.6H_2O$, is precipitated. This formula is based on the fact that when heated to 100°, six mols. of water are given off; another mol. is given off below 300°; and the final product which resists further dehydration has the composition of **molybdous diaquotetrachloroxide,** $[Mo_3Cl_4(H_2O)_2]O$. Again, when treated with hydrobromic acid, the hydroxide furnishes chlorobromides—*vide infra*—K. Lindner discussed the constitution of these compounds.

Hydrolysis occurs when either of the compounds $Mo_3Cl_6.H_2O$ or $H[Mo_3Cl_7(H_2O)].3H_2O$ is treated with water. The latter, for instance, forms a yellow soln. with the minimum quantity of cold water necessary for soln., and in a few seconds, a crystalline separation occurs forming a product with Mo : Cl=3 : 6. The product is represented as **molybdenum tetrachlorodiaquodichloride,** $[Mo_3Cl_4(H_2O)_2]Cl_2.2H_2O$; and when dehydrated, $[Mo_3Cl_4(H_2O)_2]Cl_2$, in which two of the six chlorine atoms are ionizable and replaceable by other anions. When chloroaquomolybdous acid is treated with more water, say 50 c.c. of water per 0·3 grm. of the substance, an amorphous precipitate is formed with Mo : Cl=3 : 5—**molybdenum hydroxypentachloride,** $Mo_3Cl_5(OH)$; and with a large proportion of boiling water, the amorphous precipitate has Mo : Cl=3 : 4—molybdenum diaquotetrachlorodihydroxide, $[Mo_3Cl_4(H_2O)_2](OH)_2.6H_2O$, indicated above. Ethyl alcohol also forms the 3 : 4 salt.

When chloroaquomolybdous acid is treated with pyridine and an excess of hydrogen chloride in alcoholic soln., pyridine alcoholates are formed as yellow, crystalline solids, *e.g.* with methyl alcohol, dimorphous $C_6H_5N.H[Mo_3Cl_7(H_2O)].CH_3OH$ is formed; and with ethyl alcohol, $C_6H_5N.H[Mo_3Cl_7(H_2O)].C_2H_5OH$. If the reaction occurs in amyl alcohol soln., the resulting salt, $C_6H_5N.H[Mo_3Cl_7(H_2O)]$, is free from alcohol. If this salt be crystallized from the lower alcohols, the alcoholates are formed. The mol. wt. of the pyridine salt calculated from its effect on the f.p. of nitrobenzene is 717, while 634 is required for $C_6H_5N.H[Mo_3Cl_7(H_2O)]$. The mother-liquors employed in the preparation of the alcoholates, by varying the conditions, give a series of compounds in which the anion varies from Mo : Cl=3 : 7 to 3 : 9, representing complexes of the acids $H_{1+n}[Mo_3Cl_{7+n}]$ with pyridine, etc. Thus, with a large excess of hydrogen chloride, the pyridine alcoholates $(C_6H_5N)_3H_3Mo_3Cl_9.3CH_3OH$; and $(C_5H_5N)_3H_3Mo_3Cl_9.3C_2H_5OH$; as well as $(C_6H_5N)_3H_3Mo_3O_9.C_5H_{11}OH$, were obtained, and when heated, these compounds furnish $C_5H_5N.H[Mo_3Cl_7]$ indicated above. Salts of the **heptachloromolybdous acid,** $H[Mo_3Cl_7]$, are indicated below and complexes with aniline, $C_6H_5NH_2.H[Mo_3Cl_7].9H_2O$; with urea, $Co(NH_2)_2.H[Mo_3Cl_7].3H_2O$; and with ethylenediamine, $C_2H_4(NH_2)_2.2H[Mo_3Cl_7].6H_2O$ were also obtained. Complexes of **octochloromolybdous acid,** $H_2[Mo_3Cl_8]$, were also prepared—*e.g.* with pyridine, $2C_5H_5N.H_2[Mo_3Cl_8].C_2H_5OH$; and with triaminopropane, $2C_3H_{11}N_3.3H_2[Mo_3Cl_8].45H_2O$. A. Rosenheim and F. Kohn, and K. Lindner and co-workers prepared complexes with **enneachloromolybdous acid,** $H_3[Mo_3Cl_9]$, namely $C_5H_5N.H_3[Mo_3Cl_9]$-H_2O; $3C_5H_5N.H_3[Mo_3Cl_9].3CH_2OH$; $3C_5H_5N.H_3[Mo_3Cl_9].C_2H_5OH$; and $3C_5H_5N.H_3[Mo_3Cl_9].C_5H_{11}OH$. K. Lindner also prepared still higher complexes of the acids $H_{3+n}[Mo_6Cl_{15+n}]$ with pyridine. Thus, **pentadecachloromolybdous acid,** $H_3[Mo_6Cl_{15}]$, furnishes $3C_5H_5N.H_3[Mo_6Cl_{15}].2H_2O$, $4C_5H_5N.H_3[Mo_6Cl_{15}]$, and $5C_5H_5N.H_3[Mo_6Cl_5].2C_2H_5OH$; and **heptadecamolybdous acid,** $H_5[Mo_6Cl_{17}]$, furnishes $5C_5H_5N.H_5[Mo_6Cl_{17}].2C_5H_{11}OH$.

C. W. Blomstrand reported **potassium molybdous octochloride,** $[Mo_3Cl_4]Cl_2.2KCl.2H_2O$, to be formed by evaporating a soln. of molybdenum dichloride in alkali-lye saturated with hydrogen chloride. Only half the contained chloride is precipitated by silver nitrate from the nitric acid soln. of the straw-yellow crystals. The salt is decomposed by water into potassium chloride and molybdous chloride. The corresponding **ammonium molybdous octochloride,** $[Mo_3Cl_4]Cl_2.2NH_4Cl.2H_2O$, was obtained in an analogous manner. A. Rosenheim and F. Kohn could not confirm C. W. Blomstrand's formula for the ammonium salt; and they showed that the corresponding pyridinium salt has the composition $3C_5H_5N.H_3Mo_3Cl_9.3H_2O$, as indicated above. K. Lindner, E. Haller and H. Helwig found that if a soln. of heptachloromolybdous acid, $H[Mo_3Cl_7]$, in a minimum quantity of hydrochloric acid be treated with conc. soln. of the metal chlorides, there are formed salts like **ammonium molybdous heptachloride,** $K[Mo_3Cl_7].1\frac{1}{2}H_2O$, and **potassium molybdous heptachloride,** $K[Mo_3Cl_7].3H_2O$, as well as the pyridinium salts, etc., indicated above.

J. J. Berzelius[2] prepared **molybdenum trichloride,** $MoCl_3$, and regarded it as *Molybdändichlorid,* but C. W. Blomstrand showed that it is a trichloride, and this has been confirmed by the analyses of L. P. Liechti and B. Kempe, and of A. Rosenheim and H. J. Braun. By analogy with chromic chloride, $CrCl_3$, this salt can be called **molybdic chloride,** although the affixes " ous " and " ic " are not so useful with multivalent elements which form so many compounds as in the case of vanadium and molybdenum—*vide* **9**. 54, 6. Some such system as that suggested by A. Werner is required, *e.g.* molybd**o**- for bivalent molybdenum; molybd**i**- for tervalent molybdenum; molybd**e**- for quadrivalent molybdenum; molybd**an**- for quinquevalent molybdenum; and molybd**on**- for sexivalent molybdenum.

J. J. Berzelius prepared molybdenum trichloride by passing the vapour of molybdenum pentachloride over heated molybdenum; C. W. Blomstrand said that it is not possible to obtain a homogeneous product by this process, and he recommended passing the vapour of the pentachloride, freed from oxychloride, and mixed with carbon dioxide or hydrogen through a hot tube at 250°. This method was also employed by L. P. Liechti and B. Kempe, by K. Wolf, and A. Rosenheim and H. J. Braun. A. Chilesotti obtained a red soln. of this chloride by the electrolytic reduction of a hydrochloric acid soln. of molybdenum trioxide using a mercury cathode, and a current density of 1 to 2 amp. per sq. dm.—*vide supra,* the electrolysis of molybdenum trioxide. G. G. Henderson obtained the red soln. by reduction with potassium amalgam.

A. Chilesotti showed that by varying the conc. of the acid in hydrochloric acid soln. of molybdenum trioxide, red or green soln. of molybdic chloride can be obtained, and he postulated the existence of isomerides analogous to the green and violet chromic chlorides. This hypothesis was supported by F. Förster and E. Fricke's observations on the potential of soln. of tervalent molybdenum; and by those of W. Wardlaw and R. L. Wormell on the molybdenyl chlorides—*vide infra.* The electrolysis of soln. of molybdenum trioxide in $9N$-HCl gave red or brown soln., and with $2{\cdot}7N$- to $4N$-HCl, green soln. The static potential of the red soln. is 0·12 volt at 24°–26°; and that of the green soln. under similar conditions is —0·18 volt. The red soln. are stable in air, but the green soln. are readily oxidized by air and water—especially in contact with platinum—with the evolution of hydrogen. G. Bredig and J. Michel found that the green soln. reduces perchloric acid 2000 times more quickly than the red soln.

J. J. Berzelius said that the trichloride forms a dark red powder; and L. P. Liechti and B. Kempe likened its appearance to that of red phosphorus. C. W. Blomstrand added that when sublimed, it forms a dark brick-red, crystalline, mass. W. Biltz and C. Fendius gave 3·578 for the sp. gr. at 25°/4°, and 56·6 for the mol. vol. L. P. Liechti and B. Kempe said that the trichloride is stable in dry air, and that when heated to dull redness in an atmosphere of carbon dioxide, it is decomposed into the di- and tetra-chlorides. A. Rosenheim and H. J. Braun observed that in humid air, the trichloride begins to give off hydrogen chloride, and, attracting moisture, it partly dissolves forming a brown liquid. L. P. Liechti and B. Kempe found that when heated in air, a white sublimate first appears, this becomes brownish-red, and a dark blue vapour appears—impure molybdenum dichloride remains behind. The pure trichloride was found by J. J. Berzelius, and A. Rosenheim and H. J. Braun to be insoluble in water; and L. P. Liechti and B. Kempe added that boiling water is gradually coloured brown. J. J. Berzelius said that the trichloride is decomposed by alkali-lye forming molybdic hydroxide. The trichloride is not decomposed by cold (J. J. Berzelius), or boiling (L. P. Liechti and B. Kempe) hydrochloric acid, unless, added A. Rosenheim and H. J. Braun, air has access to the liquid. L. P. Liechti and B. Kempe found that conc. sulphuric acid dissolves the trichloride forming a blue soln. which becomes emerald-green when heated. W. Wardlaw and N. D. Sylvester observed that with powdered sulphur in a soln. of tervalent molybdenum, the colour of the soln. gradually changes from green to brown, and hydrogen sulphide is evolved—particularly with warm soln. W. A. Miller said that hydrogen sulphide slowly produces a brown precipitate of hydrated molybdenum sulphide, soluble in ammonium hydrosulphide; whilst W. Wardlaw and N. D. Sylvester observed no visible effect on the green soln. of tervalent molybdenum during 2 or 3 hrs.' action, but if the sat. soln. be sealed in a flask, a black precipitate—possibly Mo_2S_3—forms in the course of a few days. A soln. of sodium tetrathionate in a soln. of tervalent molybdenum, in the presence of $3N$-H_2SO_4, in a current of nitrogen so as to remove hydrogen sulphide as it is formed, gives a brown precipitate which is a decomposition product of molybdenum tetrathionate; sodium trithionate reacts similarly. For the action of ammonia gas, *vide* molybdenum nitride, **8**. 49, 12; and molybdenum amides, **8**. 49, 21. Aq. ammonia was found by C. W. Blomstrand to act very slowly in the cold, and when heated, L. P. Liechti and B. Kempe observed that a brown powder is formed —*vide* **8**. 49, 21. The trichloride is readily dissolved by warm nitric acid. W. Hampe said that the trichloride is almost insoluble in alcohol and ether.

According to W. Wardlaw and R. L. Wormell, and in agreement with A. Chilesotti, and F. Förster and E. Fricke, the green soln. of tervalent molybdenum obtained by reducing a soln. of molybdenum trioxide in hydrochloric acid, can be made to furnish the *trihydrate* of molybdenum trichloride, $MoCl_3.3H_2O$, as well as complex salts—$R_2MoCl_5.H_2O$ and R_3MoCl_6—of tervalent molybdenum. The trihydrate was obtained in the following manner:

A soln. of 10 grms. of molybdenum trioxide in 400 c.c. of hydrochloric acid of sp. gr. 1·16, was heated on a water-bath for some hours, made up to 600 c.c., and electrolyzed in a diaphragm cell with smooth, platinum electrodes until the cathode soln. was red. This soln. was then evaporated to dryness at 70°–80° under reduced press. in an air-free flask. The residue was a copper-coloured, crystalline substance, which undoubtedly contained a portion of hydrolyzed material, and on analysis gave values of the order 1 : 2·5 for the ratio Mo : Cl. 400 c.c. of pure ether, cooled in a freezing mixture of ice and salt, and sat. with dry hydrogen chloride, were drawn into the flask by releasing the vacuum, and the red soln. obtained was evaporated to dryness under diminished press., whereupon a dark red, crystalline substance separated. In order to ensure the complete conversion of any hydrolyzed salt into the normal chloride, this operation was repeated. The substance finally obtained was quickly transferred in an atm. of dry carbon dioxide to a desiccator containing phosphoric oxide. The product was extremely hygroscopic, and exceptional precautions had to be taken to exclude moisture.

Trihydrated molybdenum trichloride separates in dark, copper-coloured crystals, very soluble in water, acetone, or cold absolute alcohol, giving intensely red solns. It rapidly reduces soln. of copper, silver, or mercuric salts. Sodium and ammonium hydroxides give black precipitates, soluble in acids; these are probably the trihydroxide. If potassium chloride is added to a soln. of the substance in alcohol, the pink complex chloride, K_2MoCl_5,H_2O, is deposited on warming.

It is not possible to get the anhydrous trichloride into aq. soln., but, as indicated above, A. Chilesotti obtained a red soln. by electrolytic reduction, and G. G. Henderson, by reduction with potassium amalgam. The evaporation of the aq. soln. gives a brown residue soluble in water and alcohol. J. J. Berzelius, and C. W. Blomstrand dissolved molybdic hydroxide in hydrochloric acid, and obtained a dark brown soln. which, on evaporation, gave a black, tough mass probably an impure oxychloride. If the red soln. is formed in the presence of alkali chlorides, complex salts are produced. These are precipitated by passing hydrogen chloride into the soln. These salts are red, or black and crystalline. They give a blue colour with ferric chloride, a dark brown colour with potassium ferricyanide, and precipitates with mercurous, lead, copper, and silver salts. G. G. Henderson could not prepare the complex salt with sodium chloride, but **ammonium molybdenum pentachloride,** $(NH_4)_2MoCl_5.H_2O$, was obtained by A. Chilesotti, and W. R. Bucknall and co-workers as a brick-red powder freely soluble in water. It was obtained by adding 25 grms. of ammonium chloride in 10 per cent. aq. soln. to 175 c.c. of a 33 per cent. soln. of molybdic chloride, concentrating the soln. under reduced press. at 70° until the bright, brick-red crystals are formed. G. Carobbi found that the crystals of the monohydrate are pleochroic, being brownish-red longitudinally and wine-red normally. The sp. gr. is 2·175 at 18°. The rhombic crystals have the axial ratios $a : b : c = 0{\cdot}6862 : 1 : 0{\cdot}71666$, and they are isomorphous with the corresponding ferric salt. Solid soln. are formed with a maximum of 90 per cent. of $(NH_4)_2FeCl_5.H_2O$. W. R. Bucknall and co-workers found that the mol. wts. of soln. with 0·863, 2·115, and 5·391 grms. of salt per 100 grms. of water were respectively 105·6, 116·8, and 141·7; and soln. with v litres per mol of water at 1° had the mol. conductivity, μ:

v	16·37	33·76	54·96	101·4	251·3
μ	107	110	132	140	175

when time=0. The conductivities increase with the age of the soln. owing to a series of hydrolytic changes resulting in the formation of molybdenyl chloride (*q.v.*). W. R. Bucknall and co-workers, F. Förster and E. Fricke, and A. Rosenheim and T. H. Li prepared **ammonium molybdenum hexachloride,** $(NH_4)_3MoCl_6.H_2O$, in rose-red needles. To prepare this salt, 80 c.c. of a soln. of 33 per cent. molybdic chloride were sat. with hydrogen chloride, added to a sat. aq. soln. of 20 grms. of ammonium chloride, and the mixture conc. to the crystallizing point. The pentachloride thus formed was removed, and the filtrate again sat. with hydrogen chloride until cold. Small rose-coloured crystals separated which, after washing free from hydrochloric acid with aq. alcohol, were dried in vacuo. G. Carobbi said that the crystals are monoclinic. W. R. Bucknall and co-workers found that an aq. soln. with 48·11, 64·44, and 157·9 grms. of the salt $(NH_4)_3MoCl_6.H_2O$, per litre at 1°, had the mol conductivities 208, 210, and 225 respectively when time=0. The conductivity increases with age owing to hydrolysis. G. Carobbi treated a soln. of 22·5 grms. of ammonium chloride with a soln. of molybdenum trichloride, and saturated it with hydrogen chloride. When the soln. was allowed to stand, it deposited monoclinic crystals of **ammonium molybdenum heptachloride,** $(NH_4)_4MoCl_7.H_2O$, of sp. gr. 1·905. A. Chilesotti, A. Rosenheim and T. H. Li, and W. R. Bucknall and co-workers obtained **potassium molybdenum hexachloride,** K_3MoCl_6, as a red powder very soluble in water. In preparing this salt, 350 c.c. of a soln. of 35 grms. of molybdenum trioxide in 8*N*-HCl were reduced to the tervalent state, conc. to 150 c.c. to make a 33 per cent. soln. of molybdic chloride, and sat. with hydrogen chloride. One-half to three-quarters of the theoretical amount of potassium chloride—30 to 40 grms.—was added as a 10 per cent. soln. in air-free water and the mixture conc. at 70° under reduced press., until crystallization commenced. The liquid was filtered and the filtrate sat. with hydrogen chloride until cold, whereupon the double salt separated. The crystals were washed with conc. hydrochloric acid, alcoholic hydrochloric acid, and finally with alcohol, and dried in vacuo. The mol. wts. of aq. soln. with 0·498, 1·470, and 3·045 were respectively 110·3, 120·5, and 167·0 by the f.p. process; and the mol. wt. decreases from 167·0 with a freshly prepared soln. to 117·3 after the lapse of 155 min. The mol. conductivities, μ, of a soln. of a mol. of the salt in v litres of water at 0°, are:

v	15·67	58·97	95·84	153·3	222·0
μ	155	195	220	230	245

when time=0. The conductivities increase with age owing to hydrolysis. D. M. Bose discussed the magnetic properties; P. Ray and H. G. Bhar found the magnetic susceptibility to be $13{\cdot}1 \times 10^{-6}$ at 25°. G. G. Henderson obtained the *dihydrate,* $K_3MoCl_6.2H_2O$, in red prisms. W. R. Bucknall and co-workers found that liquid ammonia does not react with the tripotassium molybdenum hexachloride, thus supporting the view that the ammonia replaces the molecule of water in diammonium molybdenum pentachloride. A. Chilesotti obtained a thiocyanate, $K_3Mo(CyS)_3$, by the action of potassium thiocyanate. F. Förster and E. Fricke, and W. R. Bucknall and co-workers prepared **potassium molybdenum pentachloride,** $K_2MoCl_5.H_2O$. 100 c.c. of the red soln. containing tervalent molybdenum, prepared by the electrolysis of a soln. of 10 grms. of molybdenum trioxide in 100 c.c. of $8N$-HCl, were added to 25 c.c. of a soln. of a gram of potassium chloride and the mixture was conc. in an air-free flask at 60°–70° under reduced press. to a vol. of about 20 c.c. Air-free, absolute alcohol was now admitted and a bright brick-red, crystalline precipitate separated, which, after filtration and washing with alcohol, was dried in vacuo. The mol. conductivities, μ, of soln. with a mol. of the salt in 21·19, 58·31, and 94·08 litres of water at 1° were respectively μ=113, 140, and 142; and the conductivities increase with time owing to hydrolysis. G. Carobbi found that the crystals of the pentachloride are rhombic and isomorphous with the corresponding ferric salt. The sp. gr. is 2·39 at 18°. Solid soln. with up to 83 per cent. $K_2FeCl_5.H_2O$, of sp. gr. 2·22, were formed. A soln. of the mixed salts deposits the ferrous salt $K_2FeCl_4.2H_2O$, on standing for several days. This illustrates the strong reducing action of molybdenum trichloride. W. R. Bucknall and co-workers found that ammonium molybdenum pentachloride takes up ammonia to form **ammonium molybdenum amminopentachloride,** $(NH_4)_2[MoCl_5(NH_3)].H_2O$, when 2–3 grms. of the pentachloride are treated with about 15 c.c. of liquid ammonia at the temp. of a mixture of ether and solid carbon dioxide, and the product washed first with liquid ammonia and then with dry acetone. This mauve-coloured ammine is extremely hygroscopic and undergoes rapid hydrolysis, ammonium chloride being liberated whilst the substance itself turns brown. It is readily soluble in water, producing a reddish-brown soln. from which the hydroxide separates after a few minutes. It was therefore impossible to determine its molecular conductivity. On treatment with conc. hydrochloric acid, the ammine dissolved, producing a brilliant blue coloration. On dilution, the soln. turned green and finally pink, owing, in all probability, to the re-formation of the original red complex chloride, with liberation of ammonium chloride. Attempts to isolate the blue substance were not successful. W. R. Bucknall and co-workers obtained $H[Mo(O.OC.C_6H_4.OH)_2(H_2O)]$, by the action of sodium salicylate; $Mo(OH)[C_6H_4(CO.O)_2].3H_2O$, by the action of sodium phthalate; and $Mo(OH)C_2O_4.3H_2O$, by the action of ammonium oxalate. G. Carobbi found that the ammonium and potassium salts $R_2MoCl_5.H_2O$ are isomorphous with the corresponding ferric salts $R_2FeCl_5.H_2O$. A. Chilesotti, and W. R. Bucknall and co-workers also prepared **rubidium molybdenum pentachloride,** $Rb_2MoCl_5.H_2O$, in red crystals very soluble in water; and likewise also red crystals of **cæsium molybdenum pentachloride,** $Cs_2MoCl_5.H_2O$. By using more conc. acid soln. **rubidium molybdenum hexachloride,** Rb_3MoCl_6; and **cæsium molybdenum hexachloride,** Cs_3MoCl_6, were formed. The hexahalides can be represented by the formula $R_3[MoCl_6]$, and the pentahalides by $R_2[MoCl_5(H_2O)]$. W. R. Bucknall and co-workers found that the salts of potassium and ammonium are extremely soluble even in cold water and give intensely red soln. The salts of cæsium are quite insoluble and those of rubidium nearly so. In alcohol and ether hydrolysis occurs, and this is accelerated by warming and results ultimately in the precipitation of the hydroxide of molybdenum. All the salts have pronounced reducing properties. F. Förster and E. Fricke observed that only the tervalent elements of lower atomic weight (Ti, V, Cr, Mn, Fe, Co) in this horizontal row of the periodic system appear to form easily-crystallizable complex salts with bivalent anions, whereas the elements of higher atomic weight also give well-crystallized complex salts with univalent anions. As indicated above, the formation of red or green soln. of molybdic chloride by electrolysis was found by A. Chilesotti to depend on the conc. of the hydrochloric acid. F. Förster and E. Fricke stated that the existence of the red salts, $(MoCl_6)M_3$ and $[MoCl_5.H_2O]M_2$, indicates that in the reddish-brown solns. of tervalent molybdenum an equilibrium exists between the tervalent cations and the complex ions, $(MoCl_5.H_2O)''$ and $[Mo(H_2O)_6]^{\cdots}$, respectively. Considerations of static potential lead to similar conclusions. No confirmation was obtained of Chilesotti's hypothesis of an incipient reduction of tervalent to bivalent molybdenum taking place. The presence of the ions $MoCl_6'''$, $(MoCl_5,H_2O)''$, and $[Mo,(H_2O)_6]^{\cdots}$ is held to account for the increased reducing power of the green tervalent molybdenum soln. H. J. Braun prepared complex salts with aniline, quinoline, and pyridine; and A. Rosenheim and T. H. Li, with ethylenediamine.

According to L. P. Liechti and B. Kempe,[3] when molybdenum trichloride is heated to redness in a slow current of carbon dioxide, it is resolved into molybdenum dichloride and **molybdenum tetrachloride,** $MoCl_4$, which appears as a yellow vapour, and condenses to a brown, crystalline powder which is not stable in dry carbon dioxide. When heated in a sealed tube, it decomposes into molybdenum pentachloride and trichloride, and the latter decomposes into the dichloride, etc., as indicated above—this is an extraordinary cycle. It probably means that there is a state of equilibrium between the different chlorides, and that a rise of temp. favours the lower chlorides which are less volatile. The tetrachloride is therefore one of the products of the action of chlorine on heated molybdenum; and C. W. Blomstrand, and H. Debray obtained it by the action of chlorine on a heated mixture of carbon and molybdenum oxide or sulphide. A. Michael and A. Murphy prepared the tetrachloride by heating molybdenum dioxide and carbon tetrachloride in a sealed tube at 250°. Molybdenum trioxide reacts with carbon tetrachloride at 280° with the formation of the pentachloride. When the trioxide is heated with a soln. of chlorine in carbon tetrachloride at 200°, the product consists of a yellowish-green oxychloride mixed with unchanged trioxide; at 225°, a mixture of yellow and green compounds is obtained, probably consisting of the dioxydichloride and the oxytetrachloride; at 240°, the pentachloride is produced. The pentachloride is also obtained when the oxide, Mo_3O_8, is heated with carbon tetrachloride at 240°. According to L. P. Liechti and B. Kempe, molybdenum tetrachloride is a brown, partly crystalline powder. It is affected by air as in the case of the trichloride. It does not melt when heated in a sealed tube and forms brown vapour which consists of the decomposition products as indicated above; when heated in an open tube, it forms a yellowish-white sublimate, which, owing to the action of the atm. moisture, consists of the complex oxychlorides $MoO_3.2HCl$, and MoO_2Cl_2, and chlorine and hydrogen chloride are evolved. It produces a hissing noise in contact with water; there is a vigorous reaction, and most of it forms a brown aq. soln.; alcohol, and ether behave similarly. No hydrate has been prepared; J. J. Berzelius found that a soln. of molybdenum tetrahydroxide in hydrochloric acid gives, on evaporation, a dark, amorphous, soluble mass. J. N. Pring and W. Fielding observed that the vapour of the tetrachloride, in contact with carbon, forms molybdenum or the carbide at a temp. below 1300°. There is a hissing noise produced by the action of conc. hydrochloric acid, but the boiling acid dissolves only a little tetrachloride; there is also a hissing noise produced by conc. sulphuric acid, hydrogen chloride is evolved, and a bluish-green soln. is formed. Conc. nitric acid forms a yellow soln. J. J. Berzelius evaporated a hydrochloric acid soln. of molybdenum dioxide mixed with ammonium chloride, and obtained brown crystals which C. W. Blomstrand regarded as ammonium chloride stained a brown colour. W. Wardlaw and N. D. Sylvester observed no reaction between sulphur and soln. of quadrivalent molybdenum. J. J. Berzelius saturated a hydrochloric acid soln. of molybdenum dioxide with ammonia, and obtained, on evaporation, a black, crystalline mass which formed a red soln. with water. According to C. W. Blomstrand, if a soln. of ammonium chloride is saturated with molybdenum tetrachloride, and evaporated over sulphuric acid, brown crystals of impure ammonium chloride first separate, and afterwards, green, octahedral crystals of **ammonium molybdenum tetradecachloride,**

$2NH_4Cl.3MoCl_4.6H_2O$. The salt is stable in dry air; and it decomposes when heated giving off water, ammonium chloride, hydrogen chloride, as well as molybdenum dioxide, and, if air has access, molybdenum oxychloride. The salt deliquesces in moist air. This complex salt may be an oxychloride, and not really a salt of molybdenum tetrachloride.

J. J. Berzelius,[4] and C. W. Blomstrand first prepared **molybdenum pentachloride,** $MoCl_5$; but they mistook it for *Molybdäntetrachlorid.* H. Debray showed that the product must have been the pentachloride, and this was confirmed by the analyses of L. P. Liechti and B. Kempe. According to J. J. Berzelius, chlorine gas does not act on molybdenum at ordinary temp., but when gently heated, chlorine gas freed from air and oxygen produces a transient glow over the surface of the metal, and a dark red vapour of molybdenum pentachloride is formed, and this condenses to greyish-black crystals. H. Debray distilled the product in a current of carbon dioxide in order to remove the chlorine. L. P. Liechti and B. Kempe, W. Lederer, and B. Kalischer employed an analogous mode of preparation; E. F. Smith and H. C. Burr passed chlorine over a heated mixture of molybdenum and sugar-charcoal; and C. W. Blomstrand passed dry and air-free chlorine over a mixture of molybdenum dioxide or disulphide and charcoal—the by-product, sulphur monochloride, is easily removed. P. Camboulives obtained the pentachloride by passing the vapour of carbon tetrachloride over molybdenum trioxide at 510°. A. Michael and A. Murphy's observations on this subject are indicated in connection with molybdenum tetrachloride. W. Lederer observed that when the product obtained by dissolving molybdenum in aqua regia is heated, the vapour of the pentachloride is given off. A. Chilesotti observed the presence of the pentachloride in the green soln. obtained by the electrolysis of a hydrochloric acid soln. of molybdenum trioxide (*q.v.*).

The black or greyish-black crystals of molybdenum pentachloride are very like those of iodine. The greenish tinge mentioned by H. Debray is taken by L. P. Liechti and B. Kempe to show that a trace of oxychloride is present, but O. Ruff and F. Eisner added that the crystals are dark green—almost black. C. W. Blomstrand found that the acicular crystals obtained by sublimation in carbon dioxide are dark brown or brownish-black. W. Biltz and C. Fendius gave 2·928 for the sp. gr. at 25°/4°, and 93·3 for the mol. vol. H. Debray found the vap. density at 35° to be between 9·40 and 9·53 when the theoretical value for $MoCl_3$ is 9·47. J. J. Berzelius said that the salt readily fuses; H. Debray gave 194° for the m.p., and L. P. Liechti and B. Kempe added that when the molten salt is cooled, it forms a crystalline mass. A. Michael and A. Murphy gave 194° to 195° for the m.p. H. Debray gave 268° for the b.p. C. W. Blomstrand said that when strongly heated the salt is partially decomposed. According to W. Hampe, the molten salt is dark red, and in thick layers it appears black, and if the access of moisture be prevented, it does not conduct electricity either at the m.p. or at the b.p. S. J. Lloyd found that the electrical conductivity, μ, of a mol of the salt in v litres of solvent at 18° is for the green soln. in methyl acetate $\mu=5{\cdot}1$, 3·33, and 2·88 respectively for $v=2600$, 10,400, and 41,600; for the green soln. in ethyl acetate, $\mu=1{\cdot}12$, 0·91, and 0·82 respectively for $v=3200$, 6400, and 25,600; for the olive-green soln. in acetone, $\mu=2{\cdot}02$, 2·36, and 3·75 respectively for $v=2925$, 11,700, and 103,600; for the olive-green soln. in benzaldehyde, $\mu=2{\cdot}4$, 2·15, and 1·92 respectively for $v=2900$, 5800, and 23,200; for the reddish-brown soln. in pyridine, $\mu=1{\cdot}14$, 1·79, and 3·12 respectively for $v=3150$, 12,600, and 50,400; and for the reddish-brown soln. in glycerol, $\mu=0{\cdot}92$, 1·08, and 1·95 for $v=2509$, 5018, and 20,072. A. Voigt and W. Biltz found the sp. conductivity of the molten pentachloride to be $1{\cdot}8\times10^{-6}$ mho at 216°, and $7{\cdot}5\times10^{-6}$ at 258°, and W. Biltz gave for the temp. coeff. of the conductivity $0{\cdot}0_521$. The subject was discussed by W. Biltz and W. Klemm, and G. von Hevesy.

N. Parravano and C. Mazzetti observed that molybdenum pentachloride mixed with hydrogen is reduced when passed over an iron rod at 900°, forming a film of a molybdenum-iron alloy on the heated rod. J. J. Berzelius found that when the salt is kept in a vessel containing air, an oxychloride is formed, and L. P. Liechti and B. Kempe obtained a similar product by heating the pentachloride in air. The salt fumes in moist air, and, according to J. J. Berzelius, rapidly turns bluish-green, and then deliquesces to a black, bluish-green, greenish-yellow, deep red, reddish-brown, and finally yellow liquid while hydrogen chloride is evolved. The pentachloride dissolves in water vigorously giving off so much heat that the liquid boils. H. Debray said that the aq. soln. is green or brown; and L. P. Liechti and B. Kempe added that it hisses when in contact with a small proportion of water and forms a brown liquid; with a large proportion of water the soln. is colourless. M. Guichard found that in aq. soln. the pentachloride is resolved into the tetrachloride and trioxide, and the strongly acid soln. forms a blue oxide when exposed to air. J. Nordenskjöld, and B. Kalischer consider that, in all probability, the first action of water can be represented: $MoCl_5+H_2O=MoOCl_3+2HCl$. According to L. P. Liechti and B. Kempe, a little absolute alcohol dissolves the pentachloride without hissing to form a dark green soln. which becomes brown if moisture be present; absolute ether also forms a green soln. without hissing. B. Kalischer added that chloroform and carbon tetrachloride form brown soln. which become green if a little water be present—*vide supra*. According to O. Ruff and F. Eisner, at ordinary temp., hydrogen fluoride converts it into a gaseous molybdenum fluoride and hydrogen chloride; hydrogen chloride turns the pentachloride emerald-green, whilst hydrochloric acid dissolves it with the evolution of much heat; nitric acid forms a colourless soln.; conc. sulphuric acid gives a bluish-green soln. which gradually turns brown and then yellow. W. Hampe observed that the pentachloride forms a green soln. with a small proportion of conc. hydrochloric acid, and a red or reddish-brown soln. with a larger proportion of acid. On electrolysis, the soln. of the pentachloride in conc. hydrochloric acid is reduced at the cathode to the trichloride, and at the anode $MoO_3.nHCl$ is formed. A. G. Page observed that molybdenum pentachloride acts as a catalyst in chlorinations. O. C. M. Davis obtained the complex *molybdenum nitrogen tetrasulphopentachloride*, $MoCl_5.N_4S_4$, by the action of nitrogen tetrasulphide on molybdenum pentachloride. H. J. Braun studied the action of ammonia on molybdenum pentachloride—*vide* the molybdenum amides. F. W. Bergstrom represented the reactions by $MoCl_5+8NH_3=Mo(NH)_2NH_2+5NH_4Cl$, and by $MoCl_5+8NH_3=Mo(NH_2)_4Cl+4NH_4Cl$. A. Piutti obtained *molybdenum phosphoryl octochloride*, $MoCl_5.POCl_3$, by the action of 3 mols of phosphorus pentachloride on a mol of molybdenum trioxide in a sealed tube at 170°; and E. F. Smith and G. W. Sargent, *molybdenum phosphorus decachloride*, $MoCl_5.PCl_5$, by using 5 mols of phosphorus pentachloride. W. Hampe observed that absolute alcohol or ether reacts vigorously with the evolution of heat, and giving of hydrogen chloride and ethyl chloride. The grass-green soln. formed with absolute alcohol gives a reddish-brown tetroxide when treated with alkali-lye. B. Kalischer said that the alcoholic soln. contains $MoOCl_3$; and he found that the pentachloride dissolves with a hissing noise in many organic liquids—*e.g.* alcohols, ethers, ketones, aldehydes, acids, acid anhydrides, esters, and amines. W. Wardlaw and H. W. Webb also observed that molybdenum pentachloride reacts vigorously with dry methyl, ethyl and benzyl alcohols, forming molybdenyl trichloride, but it does not react with phenol. Dry ether forms $MoCl_5.2(C_2H_5)_2O$, and with moist ether there is formed $MoOCl_3.2(C_2H_5)_2O$, which with hydrogen chloride furnishes $MoOCl_3.(C_2H_5)_2O$. Pyridine forms $MoOCl_5.2C_5H_5N$, as well as $MoCl_4.3C_5H_5N$, $MoCl_4.4C_5H_5N$, and $MoClH_4.5C_5H_5N$. A. Michael and A. Murphy found that the pentachloride is soluble in carbon tetrachloride. J. J. Berzelius said that molybdenum pentachloride unites with ammonium chloride, but not with sodium or potassium chloride. B. Kalischer found that an excess of alkali hydroxide forms $Mo(OH)_4$ and K_2MoO_4; and P. Klason, that the theoretical proportion of alkali hydroxide forms $MoO(OH)_3$.

E. F. Smith and H. C. Burr [5] found that metallic molybdenum rapidly acts on ferric chloride soln. with reduction of the ferric salt, and dissolves as a hexad; and they tried to prepare **molybdenum hexachloride,** $MoCl_6$, by driving the oxygen from an oxychloride of sexivalent molybdenum. Thus, molybdenyl chloride, MoO_2Cl_2, was mixed with an equivalent quantity of phosphorus pentachloride, and heated in a sealed tube, in the presence of chlorine, at 170°. On cooling, it was found that the tube contained a mass of greenish-black crystals; these, when freed from phosphorus oxychloride by distillation in a current of chlorine, yielded a product which, on analysis, gave figures approximating more to the pentachloride than to the hexachloride. The experiment was repeated, silicon tetrachloride being substituted for the phosphorus compound. The crystalline product was quickly removed to a boat, and distilled in an atmosphere of carbonic anhydride. The brown vapours condensed in the colder portions of the tube, and on analysis gave results varying between those required by the tetrachloride and the pentachloride. O. Ruff and F. Eisner heated a mixture of molybdenum pentachloride and liquid chlorine in a sealed tube for 96 hrs. at 100°, but obtained only crystals of the pentachloride.

REFERENCES.

[1] L. F. Svanberg and H. Struve, *Svenska Akad. Handl.*, **1**. 9, 1848; *Journ. prakt. Chem.*, (1), **44**. 257, 1848; *Phil. Mag.*, (3), **33**. 409, 524, 1848; C. J. Keyser, *Bidrag till kännedom om Molybden*, Upsala, 1851; C. W. Blomstrand, *Journ. prakt. Chem.*, (1), **71**. 449, 1857; (1), **77**. 96, 1859; (1), **82**. 423, 1861; W. Muthmann and W. Nagel, *Ber.*, **31**. 2009, 1898; A. Werner, *Zeit. anorg. Chem.*, **9**. 382, 1895; A. Rosenheim and F. Kohn, *ib.*, **66**. 1, 1910; I. Koppel, *ib.*, **77**. 289, 1912; W. Biltz, *ib.*, **166**. 275, 1927; W. Biltz and C. Fendius, *ib.*, **172**. 385, 1928; C. Fendius, *Zur Volumschemie und Verwandtschaftslehre der Uran-, Wolfram-, und Molybdänchloride*, Leipzig, 1928; L. P. Liechti and B. Kempe, *Liebig's Ann.*, **170**. 351, 1873; K. Wolf, *Das elektrochemische Verhalten des Molybdäns und einiger Molybdänverbindungen*, Aachen, 1917; A. Atterberg, *Akad. Afhandl. Upsala*, 1, 1872; *Nägra Bidrag till kännedomen om Molybdän*, Upsala, 1872; *Bull. Soc. Chim.*, (2), **18**. 21, 1872; W. Hampe, *Chem. Ztg.*, **12**. 5, 1888; K. Lindner and H. Feit, *Zeit. anorg. Chem.*, **137**. 66, 1924; K. Lindner, E. Haller, and H. Helwig, **130**. 209, 1923.

[2] J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817; *Ann. Chim. Phys.*, (2), **17**. 5, 1921; *Pogg. Ann.*, **4**. 153, 1825; **6**. 331, 369, 1826; **7**. 261, 1826; C. W. Blomstrand, *Journ. prakt. Chem.*, (1), **71**. 449, 1857; (1), **77**. 96, 1859; (1), **82**. 423, 1861; L. P. Liechti and B. Kempe, *Liebig's Ann.*, **170**. 351, 1873; A. Rosenheim and H. J. Braun, *Zeit. anorg. Chem.*, **46**. 311, 1905; H. J. Braun, *Untersuchungen über das Molybdän*, Berlin, 1904; W. Biltz and C. Fendius, *Zeit. anorg. Chem.*, **172**. 385, 1928; C. Fendius, *Zur Volumschemie und Verwandtschaftslehre der Uran-, Wolfram-, und Molybdänchloride*, Leipzig, 1928; F. Förster and E. Fricke, *Zeit. angew. Chem.*, **36**. 458, 1923; A. Rosenheim and T. H. Li, *Ber.*, **56**. B, 2228, 1923; A. Chilesotti, *Zeit. Elektrochem.*, **12**. 148, 159, 173, 182, 197, 1906; *Atti Accad. Lincei*, (5), **12**. ii, 22, 67, 1903; *Gazz. Chim. Ital.*, **33**. ii, 349, 1903; **34**. ii, 493, 1904; G. Carobbi, *ib.*, **58**. 35, 1928; W. A. Miller, *Elements of Chemistry*, London, **2**. 714, 1878; G. Bredig and J. Michel, *Zeit. phys. Chem.*, **100**. 136, 1922; W. Hampe, *Chem. Ztg.*, **12**. 5, 1888; G. G. Henderson, *Proc. Chem. Soc.*, **19**. 245, 1903; K. Wolf, *Das elektrochemische Verhalten des Molybdäns und einiger Molybdänverbindungen*, Aachen, 1917; D. M. Bose, *Zeit. Physik*, **43**. 864, 1927; A. Werner, *Neuere Anschauungen auf dem Gebiete der anorganischer Chemie*, Braunschweig, 12, 1905; London, 74, 1911; W. Wardlaw and R. L. Wormell, *Journ. Chem. Soc.*, **195**. 2370, 1924; 130, 1089, 1927; W. R. Bucknall, S. R. Carter, and W. Wardlaw, *ib.*, 512, 1927; W. Wardlaw and N. D. Sylvester, *ib.*, **123**. 969, 1923; P. Ray and H. G. Bhar, *Journ. Indian Chem. Soc.*, **5**. 497, 1928.

[3] J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817; *Ann. Chim. Phys.*, (2), **17**. 5, 1921; *Pogg. Ann.*, **4**. 153, 1825; **6**. 331, 369, 1826; **7**. 261, 1826; C. W. Blomstrand, *Journ. prakt. Chem.*, (1), **71**. 449, 1857; (1), **77**. 96, 1859; (1), **82**. 423, 1861; L. P. Liechti and B. Kempe, *Liebig's Ann.*, **170**. 351, 1873; H. Debray, *Compt. Rend.*, **46**. 1098, 1858; A. Michael and A. Murphy, *Amer. Chem. Journ.*, **44**. 365, 1910; J. N. Pring and W. Fielding, *Journ. Chem. Soc.*, **95**. 1504, 1909; W. Wardlaw and N. D. Sylvester, *ib.*, **123**. 960, 1923.

[4] J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817; *Ann. Chim. Phys.*, (2), **17**. 5, 1921; *Pogg. Ann.*, **4**. 153, 1825; **6**. 331, 369, 1826; **7**. 261, 1826; C. W. Blomstrand, *Journ. prakt. Chem.*, (1), **71**. 449, 1857; (1), **77**. 96, 1859; (1), **82**. 423, 1861; L. P. Liechti and B. Kempe, *Liebig's Ann.*, **170**. 351, 1873; K. Wolf, *Das elektrochemische Verhalten des Molybdäns und einiger Molybdänverbindungen*, Aachen, 1917; K. Lindner, E. Haller and H. Helwig, *Zeit. anorg. Chem.*, **130**. 209, 1923; A. Voigt and W. Biltz, *ib.*, **133**. 277, 1924; W. Biltz, *ib.*, **133**. 306, 1924; H. Debray, *Compt. Rend.*, **66**. 732, 1868; P. Camboulives, *ib.*, **150**. 175, 1910; C. H. Ehrenfeld, *Journ. Amer. Chem. Soc.*, **17**. 381, 1895; F. W. Bergstrom, *ib.*, **47**. 2317, 1925; E. F. Smith and H. C. Burr, *ib.*, **16**. 577, 1894; M. Guichard, *Ann. Chim. Phys.*, (7), **23**. 507, 1901; *Bull. Soc. Chim.*, (3), **25**. 188, 1901; J. Nordenskjöld, *Ber.*, **34**. 1572, 1901; P. Klason, *ib.*, **34**. 148, 1901; R. Reith, *ib.*, **3**. 668, 1870; O. Ruff and F. Eisner, *ib.*, **38**. 747, 1905; S. J. Lloyd, *Journ. Phys. Chem.*, **17**. 592, 1913; A. Michael and A. Murphy, *Journ. Amer. Chem. Soc.*, **44**. 365, 1910

W. Lederer, *Darstellung und Untersuchungen reinen geschmolzen Molybdäns*, München, 1911; B. Kalischer, *Zur Kenntnis der Halogenide des höherwertigen Wolframs und Molybdäns*, Berlin, 1902; A. Chilesotti, *Zeit. Elektrochem.*, **12**. 148, 159, 173, 182, 197, 1906; *Atti Accad. Lincei*, (5), **12**. ii, 22, 67, 1903; *Gazz. Chim. Ital.*, **33**. ii, 349, 1903; **34**. ii, 493, 1904; W. Hampe, *Chem. Ztg.*, **12**. 5, 1888; A. Piutti, *Gazz. Chim. Ital.*, **9**. 538, 1879; H. J. Braun, *Untersuchungen über das Molybdän*, Berlin, 1904; E. F. Smith and G. W. Sargent, *Zeit. anorg. Chem.*, **6**. 384, 1894; W. Biltz and W. Klemm, *ib.*, **152**. 267, 1926; W. Biltz, *ib.*, **193**. 321, 1930; W. Biltz and C. Fendius, *ib.*, **172**. 385, 1928; C. Fendius, *Zur Volumschemie und Verwandtschaftslehre der Uran-, Wolfram-, und Molybdänchloride*, Leipzig, 1928; O. C. M. Davis, *Journ. Chem. Soc.*, **89**. 1575, 1906; A. G. Page, *Liebig's Ann.*, **225**. 196, 1884; N. Parravano and C. Mazzetti, *Rec. Trav. Chim. Pays-Bas*, **42**. 821, 1923; G. von Hevesy, *Zeit. Elektrochem.*, **34**. 463, 1928; W. Wardlaw and H. W. Webb, *Journ. Chem. Soc.*, 2100, 1930.

[5] E. F. Smith and H. C. Burr, *Journ. Amer. Chem. Soc.*, **16**. 577, 1894; O. Ruff and F. Eisner, *Ber.*, **38**. 742, 1905.

§ 20. Molybdenum Oxychlorides

According to W. Wardlaw and R. L. Wormell,[1] **molybdanyl chloride**, $MoOCl.4H_2O$, can be isolated from a conc. soln. of tervalent molybdenum.

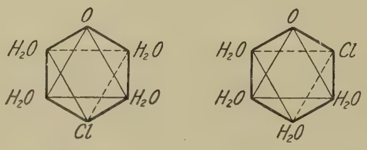
A soln. of 60 grms. of molybdenum trioxide in 390 c.c. of hydrochloric acid of sp. gr. 1·16 was heated on a water-bath for 8 hours, made up to 600 c.c., and electrolyzed, in a diaphragm cell with smooth platinum electrodes until the cathode soln. was olive-green. This soln. was then conc. at 50° under diminished press., in an air-free flask; the colour changed from green to reddish-brown at about 250 c.c. After conc. to 180–200 c.c., the soln. was transferred to a small cell and re-electrolyzed. A soln. was thus obtained having a much higher conc. of tervalent molybdenum than one prepared by direct dissolution of the trioxide in conc. hydrochloric acid. The electrolysis was continued until a sample of the cathode liquid, poured into acetone, gave an appreciable buff-coloured precipitate. The cathode soln. was now forced by the press. of carbon dioxide into air-free acetone; the oxychloride, which separated as a heavy, buff-coloured powder in almost quantitative yield, was washed with acetone, alcohol and dry ether, all these operations being performed in an atmosphere of carbon dioxide with rigid exclusion of air, and transferred to a desiccator filled with carbon dioxide, which was then evacuated. The analysis corresponds with $MoOCl.3H_2O$, but the salt was dried in a desiccator. If the oxychloride be precipitated from a soln. of about a quarter the concentration here indicated, the analysis corresponds closely with $MoOCl.4H_2O$.

It is assumed that the formation of molybdenyl chloride in aq. soln. of potassium molybdenum hexachloride is a result of a series of hydrolytic reactions $R_3[MoCl_6] + H_2O \rightleftharpoons R_2[MoCl_5(H_2O)] + RCl$; $R_2[MoCl_5(H_2O)] + H_2O \rightleftharpoons R[MoCl_4(H_2O)_2] + RCl$; $R[MoCl_4(H_2O)_2] + H_2O \rightleftharpoons MoCl_3.3H_2O + RCl$; $MoCl_3.nH_2O \rightleftharpoons MoCl_2(OH) + HCl + (n-1)H_2O$; and $MoCl_2(OH) \rightleftharpoons MoOCl + HCl$. The mol. wt. of molybdenyl chloride calculated from the f.p. of aq. soln. containing 0·1682 and 0·2531 grm. of salt in 10 grms. of water was respectively 186·1 and 191·3. The salt is thus in all probability hydrolyzed in aq. soln.; $[MoOCl.4H_2O] + H_2O \rightleftharpoons [MoO.5H_2O]^{\cdot} + Cl'$. The hydrolysis thus yields a binary electrolyte. The progressive hydrolysis is shown by the fact that aq. soln. at 1° have a mol. conductivity $\mu=33·7$ for $v=4$ after 4 min. and $\mu=50·8$ after 220 min.; and for soln. with $v=25$, $\mu=33$, after 2 min., and after 40 min., $\mu=65·2$. The dried solid is buff-coloured; and it does not deliquesce in air, although its titration value gradually falls owing to air oxidation. It is readily soluble in water and in conc. hydrochloric acid, yielding amber and reddish-brown soln. It is insoluble in acetone or ether, but dissolves slightly in cold, and readily in hot absolute alcohol. Cupric and mercuric chlorides are reduced to the " ous " condition, with further reduction to the metal by use of excess of the oxychloride. Ferric chloride also is readily reduced to the " ous " state. Sulphur, on boiling with a soln. of the solid, yields hydrogen sulphide. Sodium and ammonium hydroxides give black, flocculent precipitates, readily soluble in acids, which are probably the trihydroxides. Potassium cyanide reacts similarly. Potassium ferricyanide gives a deep red coloration. Silver nitrate is reduced to the metal, whilst lead acetate acidified with acetic acid gives no precipitate of lead chloride, indicating the absence of the chloride ion. Tungsten and uranium do not yield analogues of molybdanyl monochloride, but vanadium, which should resemble it by reason of its diagonal position in the periodic table, forms a brown, insoluble oxychloride, VOCl. An oxychloride of chromium, $CrCl(OH)_2$, has been described, but the general method of preparation of tervalent chromium oxychlorides is not satisfactory.

A green modification of molybdanyl chloride, $MoOCl.4H_2O$, has also been prepared:

A soln. of 60 grms. of molybdenum trioxide in 390 c.c. of hydrochloric acid of sp. gr. 1·16, was diluted to 500 c.c., electrolyzed for 4 hours in a diaphragm cell and concentrated at 50° under diminished press. to 250 c.c. This conc. soln., in which the molybdenum was quinquevalent, was then re-electrolyzed. On prolonged electrolysis, the soln. because green and the conc. of "free" acid diminished. At this stage, a portion of the soln., on being poured into acetone, gave a bluish-green precipitate, a typical hydrolyzed product. The cell was now cooled in ice, and the cathode liquid forced by the press. of carbon dioxide into an equal vol. of ice-cold $10N$- hydrochloric acid. The olive-green soln. thus produced was poured into air-free acetone and a green solid then separated in excellent yield. It was filtered off, washed with acetone, and dried in a vacuum desiccator. All these operations were performed in an atmosphere of carbon dioxide, air being rigidly excluded.

The mol. wts. calculated from the depression of the f.p. of water containing 0·2302 and 0·9774 grm. of the salt in 10 grms. of water were respectively 161·7 and 191·4. The mol. conductivities of a soln. with $v=5·7$ at 1° were 42·77 after the lapse of one minute, and 53·6 after the lapse of 7 min. The freshly-precipitated solid is green, but on drying it becomes greyish-green. On exposure to the air, it darkens in colour and hydrolyzes. It is more readily soluble in water and in conc. hydrochloric acid than its brown isomeride, but is insoluble in alcohol. It has similar reducing properties to the brown oxychloride, but is much more reactive. The results agree with the assumption that the two isomerides have the co-ordination formula $[MoOCl.4H_2O]$; and the reactions with sodium salicylate favour the assumption that the red and green modifications are respectively *cis-* and *trans-* isomerides:



Trans- or green form. *Cis-* or red form.

W. Wardlaw and R. L. Wormell showed that by double decomposition of the theoretical amounts of molybdanyl monochloride and the alkali salts of benzoic, tartaric, and phosphoric acids, respectively, in air-free, aq. soln., reactions occur in accordance with the equations: $MoOCl+C_6H_5.CO_2Na=C_6H_5.CO_2.MoO+NaCl$; $2MoOCl+NaKC_4H_4O_6=(MoO)_2C_4H_4O_6+NaCl+KCl$; $3MoOCl+Na_2HPO_4=(MoO)_3PO_4+2NaCl+HCl$. These insoluble molybdanyl salts are all buff-coloured and undergo gradual hydrolysis in contact with water. They are best purified by washing with dil. soln. of the corresponding acids. Soln. of sodium oxalate and normal sodium citrate also give well-defined, buff precipitates when they are added to a soln. of molybdanyl chloride. These precipitates are probably the corresponding molybdanyl salts.

W. R. Bucknall and co-workers prepared **potassium molybdenum dichloride,** $KMoOCl_2.3H_2O$, in the following manner: 350 c.c. of the green soln. containing 35 grms. of molybdenum trioxide were conc. to about 120 c.c., and re-electrolyzed for an hour to ensure the complete reduction of the molybdenum to the tervalent form. 250 c.c. of a 10 per cent. soln. of potassium chloride were added, and the whole was conc. nearly to dryness under reduced press. at 70°. The red salt formed was then removed and the filtrate treated with alcohol, whereby a bright yellow substance was precipitated. This was filtered, washed with alcohol, and dried in vacuo. It was slowly soluble in water to a reddish-brown soln., and after a time the solid turned greenish-brown. The mol. conductivity increased with time, and agreed with the assumption that the co-ordination formula is $K[MoOCl_2(H_2O)_3]$. The salt is rapidly hydrolyzed in aq. soln. By similarly treating a green soln. with ammonium chloride, an impure **ammonium molybdenum chloride,** probably $(NH_4)[Mo(OH)Cl_3(H_2O)_2]$, was formed.

It is doubtful if **molybdenyl trichloride,** $MoOCl_3$, has been prepared, although complex salts, $RCl.MoOCl_3$, are known. C. W. Blomstrand[2] obtained a product of the composition $Mo_9O_8Cl_{32}$, by the action of chlorine on an intimate mixture of molybdenum dioxide and carbon heated by an alcohol lamp; and also by passing chlorine over incompletely reduced molybdenum oxide. I. Nordenskjöld regarded the product as a mixture of MoO_2Cl_2 and $MoCl_5$; and P. Klason, as molybdenyl trichloride. C. W. Blomstrand described it as a dark green mass of tabular crystals; it melts and vaporizes below 100°. It is stable when heated in a sealed tube, and in thin layers in direct sunlight, it acquires a reddish colour. It quickly decomposes when exposed to air and becomes blue. It can be sublimed in hydrogen. The vapour is dark reddish-brown. It is vigorously attacked by water; it forms a green soln. with a small proportion of water—a single drop of water colours it blue—and with more water a blue precipitate is formed. H. Fleck and E. F. Smith found that the compound reacts with ethylamine; and I. Nordenskjöld obtained complexes by adding aliphatic amines or pyridine to the soln. in hydrochloric acid. This soln. is supposed to contain $MoOCl_3.2HCl$, or $H_2[MoOCl_5]$, for, with alkali or organic ammonium chlorides, it yields complex salts of the type $R_2[MoOCl_5)$. For a similar reason, green soln. of molybdenum pentachloride are supposed to contain molybdenyl trichloride. If the green soln. is diluted with water, it becomes brown owing to the formation of colloidal $Mo(OH)_5$, but when hydrochloric acid is added the soln. becomes green. J. J. Berzelius showed that a soln. of molybdenum trioxide is readily reduced by hydriodic acid, and F. Mauro and L. Danesi showed that the molybdenum trioxide is reduced to a quinquevalent form with the liberation of an atom of iodine per mol. of the trioxide. The reaction was utilized in the iodometric determination of molybdenum by C. Friedheim and H. von Euler-Chelpin, and F. A. Gooch and co-workers.

G. Bailhache prepared **ammonium molybdenyl pentachloride,** $2NH_4Cl.MoOCl_3$, or $(NH_4)_2[MoOCl_5]$, by crystallization from a soln. of potassium molybdenyl oxalate and ammonium chloride in hydrochloric acid; and by passing hydrogen chloride into a soln. of molybdenum trioxydisulphate, $Mo_2O_3(SO_4)_2$, and ammonium chloride. P. Klason also obtained this salt by adding a mol of ammonium iodide, and 0·1 mol ammonium chloride per gram-atom of molybdenum, to a soln. of 200 grms. of ammonium molybdate in 600 c.c. of fuming hydrochloric acid; distilling off the iodine on a sand-bath with fresh additions of hydrochloric acid; and saturating the liquid with hydrogen chloride. The green liquid was allowed to stand for crystallization. F. Förster and E. Fricke obtained the salt by electrolytically reducing a soln. of molybdenum trioxide in hydrochloric acid, and subsequently adding ammonium chloride to the liquid. R. G. James and W. Wardlaw used the following process:

> 100 grms. of molybdenum trioxide were dissolved in 500 c.c. of hot hydrochloric acid of sp. gr. 1·16, and the soln. evaporated to 250 c.c., filtered, and made up to 500 c.c. with hydrochloric acid. 150 c.c. of this liquid were placed in a diaphragm cell containing $10N$-NH_4OH and a small quantity of ammonium chloride. On electrolysis with a current density of 0·1 amp. per sq. cm., and continuous saturation of the cathode with hydrogen chloride, a good yield of the salt separated out.

The lowering of the f.p. of aq. soln. agrees with a mol. wt. of about 36 when the mol. wt. of $(NH_4)_2MoCl_5$ is 325·3. The electrical conductivities of soln. with a mol of the salt in 199·2, 796·8, 1593·6, and 3187·2 litres of water are, respectively, 755·3, 865·6, 916·8, and 948. The results are taken to agree with the assumption that the complex $MoOCl_5''$-ion is unstable and that ionization and hydrolysis occur in

accord with $R_2[MoOCl_5]+H_2O\rightleftharpoons R[MoOCl_4,H_2O]+RCl$; $R[MoOCl_4,H_2O]+H_2O \rightleftharpoons [MoOCl_3.2H_2O]+RCl$; $[MoOCl_3,2H_2O]+H_2O\rightleftharpoons[MoO(OH)Cl_2,2H_2O]+HCl$; $[MoO(OH)Cl_2.2H_2O]+H_2O=[MoO(OH)_2Cl,2H_2O]+HCl=[MoO_2Cl,3H_2O]+HCl$; $[MoO_2Cl,3H_2O]+H_2O\rightleftharpoons[MoO_2(OH),3H_2O]+HCl$. Whence at infinite dilution: $R_2[MoOCl_5]+5H_2O\rightleftharpoons[MoO_2(OH),3H_2O]+2RCl+3HCl$. This agrees with the observed fact that 10 ions per mol. are produced at infinite dilution. Additional confirmation of this scheme of ionization for the complex salts is afforded by the isolation of the intermediate products $R[MoOCl_4,H_2O]$, $R[MoO_2Cl_2,2H_2O]$, and an oxychloride, $[Mo_2O_4(OH)Cl,4H_2O]$, which may be considered as derived from the intermediate substances $[MoO_2Cl,3H_2O]$ and $[MoO_2(OH),3H_2O]$. According to P. Klason, the green, octahedral crystals are stable in air, and easily soluble in water. The salt can be reprecipitated from its aq. soln. by passing in hydrogen chloride. The salt in aq. soln. is hydrolyzed, and it may then suffer auto-reduction to form molybdenum blue. The salt is decomposed by alcohol. In addition to the green salt, H. Winkler obtained a brown form by evaporating on a water-bath the green mother-liquid from the green salt until a film of crystals appears on the surface, and cooling the liquid by ice-water. If the crystals are green, the treatment is repeated on the mother-liquid. The brown, cubic crystals are stable in air; and they are easily auto-oxidized. They form a green soln. with water—*vide infra.* A. Rosenheim and M. Koss, G. Scagliarini, R. G. James and W. Wardlaw, and J. Sand and O. K. H. Burger obtained complex salts with pyridine; and R. G. James and W. Wardlaw, salts with quinoline, and with trimethylammonium. I. Nordenskjöld prepared **potassium molybdenyl pentachloride,** $K_2MoOCl_5.2H_2O$, by adding the calculated quantity of hydriodic acid to a soln. of molybdenum trioxide in fuming hydrochloric acid, driving off the free iodine, saturating the soln. with hydrogen chloride, adding the calculated quantity of potassium chloride, and concentrating the soln. in a current of hydrogen chloride. F. Förster and E. Fricke, and R. G. James and W. Wardlaw also prepared this salt. The lowering of the f.p. of aq. soln. agrees with an apparent mol. wt. of about 40 when the theoretical value for K_2MoOCl_5 is 367·5. The electrical conductivities of soln. of a mol of the salt in 36·54, 292·3, 584·6, and 1169·3 litres of water are, respectively, 676·6, 834·3, 987·3, and 954. G. G. Henderson added potassium chloride to a conc. soln. of molybdic hydroxide in hydrochloric acid, and saturated the liquid with hydrogen chloride; and he also treated a soln. of molybdenum trioxide in hydrochloric acid with potassium amalgam. The dark green, rhombic prisms are stable in air; and when it is treated in hydrochloric acid soln. with potassium amalgam, $K_3MoOCl_6.2H_2O$ is formed. I. Nordenskjöld prepared **rubidium molybdenyl pentachloride,** Rb_2MoOCl_5, in a similar manner, and obtained green, rhombic octahedral crystals, which are less soluble than the potassium salt. This salt was also prepared by F. Förster and E. Fricke, and by R. G. James and W. Wardlaw as indicated above. The lowering of the f.p. of aq. soln. agrees with an apparent mol. wt. of about 36 when the theoretical value for Rb_2MoOCl_3 is 460·3. The electrical conductivities of soln. with a mol of the salt in 51·14, 409·1, 818·2 and 1636·4 litres of water are, respectively, 688, 849, 910, and 973. I. Nordenskjöld prepared sparingly soluble **cæsium molybdenyl pentachloride,** Cs_2MoOCl_5, which forms yellowish-green, rhombic, octahedral, sparingly-soluble crystals. The salts R_2MoOCl_5, generally crystallize in the rhombic system, and range in colour from dark green through shades of emerald-green to yellowish-green. The pyridine salt exhibits a strong pleochroism and has a very high double refraction. When exposed to a moist atm., these salts more or less rapidly turn reddish-brown, in which condition they are very susceptible to aërial oxidation, molybdenum blue being formed. The pyridinium and the ditrimethylammonium salts give a bright copper-red substance at one stage of these changes. The potassium and the substituted-ammonium salts are the most sensitive, and the quinolinium the least sensitive, to the action of moist air. All the complex salts are soluble in water, the conc. soln. being reddish-brown, passing through orange to bright yellow on dilution. On sat. with hydrogen chloride, these aq. soln. finally turn emerald-green and from sufficiently conc. soln. the complex salts separate. Alcohol dissolves all these green salts, and from the soln. of the alkali complex salts, alkali chlorides separate on heating. The pyridinium salt under these conditions yields a red precipitate, which will be referred to in detail later. The addition of pyridine or quinoline to aq. soln. of any of the complex salts gives a brown, insoluble precipitate.

R. G. James and W. Wardlaw prepared **trimethylammonium molybdenyl tetrachloride,** $R[MoOCl_4(H_2O)]$, as follows: 75 c.c. of the soln. of molybdenum oxide, indicated above, were electrolytically reduced to the quinquevalent stage, and were concentrated on a water-bath under diminished press. to 20–25 c.c. Thirty c.c. of a soln. of 11 grms. of trimethylamine hydrochloride were now admitted by releasing the vacuum, and the mixture was heated to boiling under diminished press. The soln. was then sat. with hydrogen chloride while it was being cooled, finally in a freezing-mixture, and the emerald-green crystals thus obtained were filtered, washed with conc. hydrochloric acid, and dried in a vacuum over solid potassium hydroxide and phosphoric oxide. The mol. wt. by the cryoscopic process is about 47, when the mol. wt. of $(CH_3)_3HNMoOCl_4H_2O$ is 331·8. The mol. conductivity, μ, of a soln. in v litres of water is:

v . .	35·6	71·2	142·4	284·8	569·6	1139·2	2278·4	4556·8
μ . .	580	614	657	706	773	852	849	874

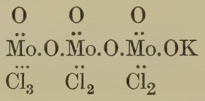
The calculated value for μ_∞ at 0° is nearly 880, on the scheme of ionization and hydrolysis indicated above, when there are 8 ions produced per mol.

According to J. Sand and O. K. Burger, when green **pyridine molybdenyl pentachloride** is boiled with alcohol and cooled there separate out copper-red crystals of pyridinium molybdenyl dichloride, $C_5H_6N.MoO_2Cl_2.2H_2O$. The salt was also prepared by R. G. James and W. Wardlaw. The mol. wt. by cryoscopic methods ranges from 61·6 to 86·06 when the value for $C_5H_6N.MoO_2Cl_2(H_2O)$ is 296·9. The mol. conductivity, μ, at 0°, of a soln. of a mol of the salt in v litres is:

v . .	20·56	41·12	164·5	329	1316
μ . .	185	210·6	275·1	312·0	336·0

These results are explained by the assumption that in aq. soln. the pyridinium salt undergoes ionization and hydrolysis in accordance with the scheme: $MoO_2Cl_2,2H_2O + C_5H_6N + H_2O \rightleftharpoons C_5H_6NCl + MoO_2Cl + 2H_2O \rightleftharpoons C_5H_6N^{\cdot} + Cl' + MoO_2Cl.3H_2O$; $MoO_2Cl.3H_2O + H_2O \rightleftharpoons MoO_2(OH),3H_2O + H^{\cdot} + Cl'$. R. G. James and W. Wardlaw prepared **molybdenum tetroxyhydroxychloride,** $Mo_2O_4(OH)Cl.4H_2O$—mol. wt. 380·5—as follows: The reddish-brown soln. of quinquevalent molybdenum, obtained by the electrolytic reduction of 150 c.c. of molybdic acid soln., was conc. on a water-bath under diminished press. until a dark, viscous mass was obtained. Pure, dry acetone was admitted in small portions with frequent shaking and warming, until the mass just dissolved, giving a deep brown soln. This was poured with constant stirring into a large volume of dry ether and a bulky reddish-brown precipitate separated, which was washed with dry ether and kept over solid potassium hydroxide in vacuo. This salt is a reddish-brown powder, readily soluble in water and in alcohol, giving deep reddish-brown soln. which on dilution become bright yellow. The aq. soln. is acid to litmus and reduces soln. of silver salts. The brown aq. or alcoholic soln. of the compound turn emerald-green on saturation with hydrogen chloride, and complex salts of the type R_2MoOCl_5 may be isolated from them. On heating, the chloride decomposes with evolution of hydrogen chloride. The mol. wt. by the cryoscopic process is 157·9 to 205·7. These results indicate that two ions are present in the more conc. soln. and three individuals in the more dil. This is satisfactorily explained by the progressive hydrolysis $Mo_2O_4(OH)Cl + H_2O \rightleftharpoons Mo_2O_4(OH),H_2O + Cl \rightleftharpoons Mo_2O_4(OH),H_2O^{\cdot} + Cl'$ or $Mo_2O_4(OH)Cl + H_2O \rightleftharpoons Mo_2O_4(OH)_2 + H^{\cdot} + Cl'$.

H. Rose,[3] and J. J. Berzelius prepared **molybdenum dioxydichloride,** MoO_2Cl_2, as a sublimate by the action of dry chlorine on heated molybdenum dioxide ; and also by heating a mixture of molybdenum trioxide, potassium hydrosulphate, and sodium chloride ; W. Püttbach, and O. Ruff and F. Eisner, by passing chlorine over a heated mixture of molybdenum trioxide and carbon ; and C. W. Blomstrand, by the action of oxygen on molybdenum chloride or oxychloride, or by exposing the substances to moist air in the cold. According to C. W. Blomstrand, the yellowish-white, scaly crystals in the presence of some of the other oxychlorides may produce a red coloration. The crystals have a bitter, and acidic taste. The salt volatilizes without melting, but it can be melted in a sealed tube. It is hydrolyzed by water, $MoO_2Cl_2+H_2O=MoO_3+2HCl$. A. W. Cronander observed that with phosphorus pentachloride, *molybdenum diphosphotetradecachloride*, $MoCl_4.2PCl_5$, is formed. The salt is soluble in water, alcohol, and ether. W. Hampe said that the soln. in alcohol is an electrical conductor, but the soln. in ether is a non-conductor unless a trace of water be present. Hydrogen reduces the salt to molybdenum dioxide. E. Weinland and W. Knöll obtained six-sided plates of **ammonium molybdenum dioxytetrachloride,** $2NH_4Cl.MoO_2Cl_2.2H_2O$, or $Mo(ONH_4)_2Cl_4.2H_2O$, or $(NH_4)_2[MoO_2Cl_4].2H_2O$, from a soln. of molybdenum trioxide in conc. hydrochloric acid, saturated with ammonium chloride ; greenish-yellow, six-sided plates of **potassium molybdenum dioxytetrachloride,** $K_2[MoO_2Cl_4].2H_2O$, were obtained in a similar way from soln. with $MoO_3 : KCl=1 : 1$; likewise with six-sided plates of **rubidium molybdenum dioxytetrachloride,** $Rb_2[MoO_2Cl_4]$, and yellowish-green, hygroscopic crystals of **cæsium molybdenum dioxytetrachloride,** $Cs_2[MoO_2Cl_4]$. The salts are hydrolyzed by water. The mother-liquor obtained in preparing the potassium salt also furnishes six-sided plates of **potassium molybdenum dioxytrichloride,** $K[MoO_2Cl_3(H_2O)]$, or $MoCl_3(OK).(OH)_2$, and the same salt is deposited by soln. with $MoO_3 : KCl=3 : 1$; and similarly with **rubidium molybdenum dioxytrichloride,** $Rb[MoO_2Cl_3(H_2O)]$, and **cæsium molybdenum dioxytrichloride,** $Cs[MoO_2Cl_3(H_2O)]$. The mother-liquor employed in the preparation of the potassium salt furnishes aggregates of prisms of **potassium trimolybdenum dioxyheptachloride,** $KCl.3MoO_2Cl_2$, or $K[Mo_3O_6Cl_7].3H_2O$; and similarly with **cæsium trimolybdenum dioxyheptachloride,** $CsCl.3MoO_2Cl_2.11H_2O$, which is also obtained from a hydrochloric acid soln. with $MoO_3 : CsCl=8$ to $12 : 1$. The prismatic crystals are very hygroscopic. The constitution of these salts can be represented by :



$$\underset{\overset{\cdot\cdot\cdot}{\mathrm{Cl_3}}}{\overset{\mathrm{O}}{\ddot{\mathrm{Mo}}}}\mathrm{.O.}\underset{\overset{\cdot\cdot}{\mathrm{Cl_2}}}{\overset{\mathrm{O}}{\ddot{\mathrm{Mo}}}}\mathrm{.O.}\underset{\overset{\cdot\cdot}{\mathrm{Cl_2}}}{\overset{\mathrm{O}}{\ddot{\mathrm{Mo}}}}\mathrm{.OK}$$

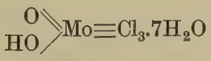
W. Püttbach [4] reported **molybdenum oxytetrachloride,** $MoOCl_4$, to be formed by the action of molybdenum pentachloride on molybdenum dichloride ; and by the action of chlorine on a mixture of molybdenum and its dioxide. The green, crystalline sublimate is hygroscopic, and on exposure to air acquires a red film. This compound was represented by C. W. Blomstrand by the formula $Mo_9O_8Cl_2$. P. Klason regarded it as containing $MoOCl_3$; but I. Nordenskjöld showed that it is probably a mixture of molybdenum pentachloride and molybdenum dichloride.

C. W. Blomstrand observed that in the preparation of molybdenyl trichloride, a much less volatile **molybdenum trioxyhexachloride,** $Mo_2O_3Cl_6$, is formed ; and W. Püttbach obtained the same product by repeatedly subliming molybdenyl tetrachloride in a current of carbon dioxide. The deep violet, or ruby-red crystals are stable in dry air, but they gradually decompose in moist air. The salt is hydrolyzed by water. W. Hampe found that it forms a yellow, non-conducting soln. with ether. When the violet salt is heated in a current of carbon dioxide, C. W. Blomstrand, and W. Püttbach found that *molybdenum pentoxyoctochloride*, $Mo_3O_5Cl_8$, is formed in radiating masses of red needles which are stable in air ; they are insoluble in hydrochloric acid, and in cold sulphuric acid ; and soluble in hot sulphuric acid, in nitric acid, and in aq. ammonia.

Some intermediate oxychlorides have been reported. Thus, W. Püttbach heated molybdenyl tetrachloride in a current of hydrogen, and obtained *molybdenum trioxyheptachloride*, $Mo_3O_3Cl_7$, as the chief product along with some molybdenum, and molybdenum dichloride. The dark violet, acicular crystals are treated with water to decompose the unchanged molybdenyl chloride. The brown, acicular crystals volatilize without melting, and are slightly soluble in hydrochloric acid ; and form a colourless soln. with nitric acid, or alkali-lye. W. Püttbach also said that *molybdenum trioxytetrachloride*, $Mo_2O_3Cl_4$, is obtained as an easily volatilized sublimate in the preparation of molybdenum tetrachloride. C. W. Blomstrand prepared molybdenum trioxypentachloride, $Mo_2O_3Cl_5$, by heating molybdenum hemitrioxide in dry chlorine, and subliming the product in hydrogen. The brown or brownish-black product easily melts, and it sublimes slowly giving dark reddish-brown vapours. It deliquesces in moist air forming a blue liquid. It is easily soluble in water—the soln. becomes green, and then blue. With an excess of water, a blue precipitate is formed.

H. Debray[5] prepared *molybdenum trioxybishydrochloride*, or **molybdenyl dihydroxydichloride,** or **molybdenum oxydihydroxydichloride,** $MoO_3.2HCl$, or $MoO(OH)_2Cl_2$, or, according to A. Werner, $H_2[MoO_3Cl_2]$, by passing hydrogen chloride over molybdenum trioxide at 150° to 200°. It collects as a sublimate beyond the heated zone. E. Péchard, and E. F. Smith and V. Oberholtzer obtained it by heating a non-volatile molybdate to 360°–400° in a current of hydrogen chloride. According to H. Debray, the compound forms white, or if slowly cooled, yellowish needles which are very easily volatilized in a current of hydrogen chloride, but are decomposed when heated in air. This volatility enables molybdenum to be separated from silica, tungsten trioxide, and other substances which do not form chlorides volatilizable at about 400°. A. Vandenberghe's observations on the vap. density show that the compound is somewhat dissociated at 160°. H. Debray said that the salt is easily soluble in water, and when the aq. soln. is evaporated, it deposits molybdenum trioxide. E. Péchard found that the salt is readily soluble in ether, so that it can be extracted by ether from a conc. hydrochloric acid soln. of a molybdate, and the ethereal soln. deposits crystals of an ethereal complex ; the salt is also soluble in alcohols, acetone, ether, and glacial acetic acid. B. Kalischer observed some reduction accompanied by the smell of aldehyde with the alcoholic soln. A. Vandenberghe found from the effect of the salt on the f.p. of glacial acetic acid that the mol. wt. is 114·4 to 123·0 ; acetic acid, 156·0 to 314·1 ; and water, 38·4 to 57·8 ; while its effect on the b.p. of ethyl ether agrees with the mol. wt. 208·6 to 229·0 ; acetone, 220·8 to 236·1 ; methyl alcohol, 101·3 to 121·6 ; and ethyl alcohol, 160·0 to 181·8. The data with ether and acetone are in agreement with the normal mol. wt. ; with alcohol, the salt is dissociated, and more so with methyl than with ethyl alcohol ; with water, the decomposition is great.

E. Weinland and W. Knöll found that when molybdenyl dihydroxydichloride is made into a mush with fuming hydrochloric acid, and the mixture warmed, the mass solidifies to form crystalline **molybdenum oxyhydroxytrichloride,** or **molybdenyl hydroxytrichloride,** $MoO(OH)Cl_3.7H_2O$, or



$$\left.\begin{matrix}O\\HO\end{matrix}\right>Mo\equiv Cl_3.7H_2O$$

The salt is also formed by saturating with hydrogen chloride a soln. of molybdenyl dihydroxydichloride in fuming hydrochloric acid, and evaporating the liquid over sulphuric acid ; and the salt has been found to separate from soln. containing magnesium or calcium molybdates. The pale green prisms or plates are very hygroscopic, and effloresce over sulphuric acid losing at the same time some hydrogen chloride. The salt dissolves in water without depositing molybdic acid.

C. W. Blomstrand obtained **molybdenum dihydroxytetrachloride,** $Mo_3(OH)_2.Cl_4.2H_2O$, by adding acetic acid to an alkaline soln. of molybdous chloride. The *dihydrate* is a pale yellow, amorphous salt insoluble in water, or alcohol ; it is freely soluble in strong acids if it is freshly precipitated and washed with cold water ; if washed with hot water, it is less soluble in acids. If the soln. in sulphuric or nitric acid is washed with water, it is precipitated as a compact, yellow powder which is not soluble in acids—conc. sulphuric acid or fuming nitric acid. C. W. Blomstrand obtained pale yellow crystals of the *octohydrate* by precipitation from an alkaline soln. of molybdous acid by carbon dioxide. W. Muthmann and W. Nagel obtained it at the cathode by the electrolysis of a soln. of molybdous chloride in 96 per cent. alcohol. K. Lindner and co-workers found that at 35° it can be represented by $[Mo_3Cl_4(H_2O)_2](OH)_2.H_2O$; at 67°–100°, by $[Mo_3Cl_4(H_2O)_2](OH)_2$; and at 200°–300°, it forms **molybdenum oxytetrachloride,** $[Mo_3Cl_4(H_2O)_2]O$. They also prepared a complex acetate, $[Mo_3Cl_4(H_2O)_2](C_2H_3O_2)_2$.

P. Didier [6] did not succeed in preparing **chloromolybdates** analogous to the chlorotungstates.

REFERENCES.

[1] W. Wardlaw and R. L. Wormell, *Journ. Chem. Soc.*, **125**. 2370, 1924; 130, 1087, 1927; W. R. Bucknall, S. R. Carter and W. Wardlaw, *ib.*, 512, 1927.

[2] H. Fleck and E. F. Smith, *Zeit. anorg. Chem.*, **7**. 351, 1894; C. W. Blomstrand, *Journ. prakt. Chem.*, (1), **71**. 460, 1857; I. Nordenskjöld, *Ber.*, **34**. 1572, 1901; P. Klason, *ib.*, **34**. 148, 1901; C. Friedheim and H. von Euler-Chelpin, *ib.*, **28**. 2061, 1895; F. Mauro and L. Danesi, *Gazz. Chim. Ital.*, **11**. 286, 1881; *Zeit. anal. Chem.*, **20**. 507, 1881; J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817; *Ann. Chim. Phys.*, (2), **17**. 5, 1921; *Pogg. Ann.*, **4**. 153, 1825; **6**. 331, 369, 1826; **7**. 261, 1826; F. A. Gooch and C. Fairbanks, *Amer. Journ. Science*, (4), **2**. 156, 1896; *Zeit. anorg. Chem.*, **13**. 101, 1897; F. A. Gooch and J. T. Norton, *ib.*, **18**. 312, 1898; *Amer. Journ. Science*, (4), **6**. 168, 1898; G. Bailhache, *Compt. Rend.*, **135**. 862, 1902; H. Winkler, *Ueber Verbindungen des Molybdäns mit komplexen negativen Radikalen*, Zürich, 1909; G. G. Henderson, *Proc. Chem. Soc.*, **19**. 245, 1903; A. Rosenheim and M. Koss, *Zeit. anorg. Chem.*, **49**. 148, 1906; J. Sand and O. K. Burger, *Ber.*, **39**. 1761, 1906; G. Scagliarini, *Atti Accad. Lincei*, (6), **1**. 676, 1925; A. Chilesotti, *Zeit. Elektrochem.*, **12**. 173, 1906; F. Förster and E. Fricke, *Zeit. angew. Chem.*, **36**. 458, 1923; R. G. James and W. Wardlaw, *Journ. Chem. Soc.*, 2145, 1927.

[3] J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817; *Ann. Chim. Phys.*, (2), **17**. 5, 1921; *Pogg. Ann.*, **4**. 153, 1825; **6**. 331, 369, 1826; **7**. 261, 1826; J. Sand and O. K. H. Burger, *Ber.*, **39**. 176, 1906; H. Rose, *Pogg. Ann.*, **75**. 319, 1848; R. G. James and W. Wardlaw, *Journ. Chem. Soc.*, 2145, 1927; L. F. Svanberg and H. Struve, *Svenska Akad. Handl.*, 75, 1848; *Phil. Mag.*, (3), **33**. 409, 524, 1848; *Journ. prakt. Chem.*, (1), **44**. 257, 1848; C. W. Blomstrand, *ib.*, (1), **71**. 449, 1857; W. Hampe, *Chem. Ztg.*, **12**. 23, 1888; W. Püttbach, *Liebig's Ann.*, **201**. 125, 1880; *Ueber Molybdänacichloride*, Elberfeld, 1878; O. Ruff and F. Eisner, *Ber.*, **38**. 742, 1905; E. Weinland and W. Knöll, *Zeit. anorg. Chem.*, **44**. 81, 1905; A. W. Cronander, *Bull. Soc. Chim.*, (2), **19**. 499, 1873; *Ber.*, **6**. 1466, 1873; *Oefvers. Akad. Stockholm*, **27**. 57, 1870.

[4] W. Püttbach, *Liebig's Ann.*, **201**. 125, 1880; *Ueber Molybdänacichloride*, Elberfeld, 1878; P. Klason, *Ber.*, **34**. 148, 1901; I. Nordenskjöld, *ib.*, **34**. 1572, 1901; C. W. Blomstrand, *Journ. prakt. Chem.*, (1), **71**. 449, 1857; W. Hampe, *Chem. Ztg.*, **12**. 23, 1888.

[5] H. Debray, *Compt. Rend.*, **46**. 1101, 1858; E. Péchard, *ib.*, **114**. 1358, 1892; *Ann. Chim. Phys.*, (6), **28**. 537, 1893; A. Vandenberghe, *Zeit. anorg. Chem.*, **10**. 47, 1895; A. Werner, *ib.*, **9**. 382, 1895; K. Lindner, E. Haller and H. Helwig, *ib.*, **130**. 209, 1923; E. Weinland and W. Knöll, *ib.*, **44**. 81, 1905; E. F. Smith and V. Oberholtzer, *ib.*, **4**. 236, 1893; C. W. Blomstrand, *Journ. prakt. Chem.*, (1), **77**. 100, 1859; W. Muthmann and W. Nagel, *Ber.*, **31**. 2009, 1898; B. Kalischer, *Zur Kenntnis der Halogenide des höherwertigen Wolframs und Molybdäns*, Berlin, 1902.

[6] P. Didier, *Compt. Rend.*, **102**. 823, 1886.

§ 21. Molybdenum Bromides and Oxybromides

C. W. Blomstrand [1] obtained **molybdenum dibromide,** or **molybdous bromide,** $MoBr_2$, or $(MoBr_2)_3$, by heating the tribromide to redness. If molybdenum is heated in the vapour of bromine, molybdous bromide will be found as a non-volatile residue in the part subjected to the strongest heat. It is purified by elutriation with water so as to leave the unchanged molybdenum behind. A. Atterberg obtained it by a similar process; and K. Lindner and H. Helwig, by passing nitrogen and bromine vapour over powdered molybdenum at 600° to 700°. The yellowish-red product is infusible. It is insoluble in water and acids, and even in boiling nitric acid. W. Muthmann and W. Nagel represent the bromide by the formula $[Mo_3Br_4]Br_2$. Molybdous bromide is completely decomposed by alkali-lye with the separation of black hydrated molybdic oxide, while it is freely soluble in dil. alkali-lye forming a yellow liquid containing alkali bromide and $Mo_3(OH)_2Br_4$; acids precipitate from this soln. various complexes $[Mo_3Br_4]X_2.nH_2O$, where X_2 denotes F_2, Cl_2, Br_2, I_2, SO_4, $(NO_3)_2$, $(H_2PO_4)_2$, CrO_4, MoO_4, C_2O_4, etc. If hydrobromic acid be added to $Mo_3(OH)_2Br_4$, or to $Mo_3Br_4I_2$, the trihydrate, $[Mo_3Br_4]Br_2.3H_2O$, is formed. K. Lindner discussed the constitution of these compounds. W. Lederer obtained a yellowish-white compound by the action of bromine or bromine water on molybdenum. F. W. Bergstrom studied the action of liquid ammonia and obtained an ammoniobasic halide. K. Lindner and H. Helwig prepared **molybdous amminobromide,** $Mo_3Br_6(NH_3)_2.C_2H_5OH$, as well as a complex with pyridine, $Mo_3Br_6.C_5H_5N$. The action of alcoholic halogen acids furnishes the pyridine salt of **hydrobromomolybdous acids,** $C_5H_5N.HMo_3Br_7$; $(C_5H_5N)_5H_5Mo_6Br_{17}.2C_2H_5OH$; and also salts of mixed hydrobromochloromolybdous acids.

C. W. Blomstrand[2] prepared **molybdenum tribromide,** or **molybdic bromide,** $MoBr_3$, by passing the vapour of bromine over molybdenum or a mixture of molybdenum dioxide and carbon heated by an alcohol lamp; and A. Rosenheim and H. J. Braun obtained it by passing dry carbon dioxide mixed with the vapour of dry bromine over warm molybdenum, and as a brownish-red soln. by the electrolytic reduction of a soln. of 37 grms. of hydrated molybdic acid in 240 c.c. of conc. hydrobromic acid by a current of 0·6 to 0·8 amp. The tribromide forms a dark green or black mass of acicular crystals. It volatilizes with difficulty, and when strongly heated yields bromine and the dibromide. It is insoluble and not decomposed by water; ammonia gas transformed it at a low temp. into molybdenum; boiling hydrochloric acid, and cold dil. nitric acid do not attack it perceptibly; dil. alkali-lye acts slowly in the cold, whilst the boiling lye transforms it into hydrated oxide. F. W. Bergstrom studied the action of liquid ammonia, and obtained a deep red soln. and an ammoniobasic bromide. When a soln. of the salt is treated with ammonium bromide, and evaporated, A. Rosenheim and H. J. Braun obtained black rhombic crystals of **ammonium molybdenum pentabromide,** $(NH_4)_2MoBr_5.H_2O$. The salt is very soluble in water, forming a blood-red soln. F. Förster and E. Fricke represented it by $(NH_4)_2[MoBr_5(H_2O)]$. W. Wardlaw and A. J. I. Harding prepared **potassium molybdenum pentabromide,** K_2MoBr_5, by adding 20 c.c. of a soln. of 1·5 grms. of potassium bromide to 100 c.c. of a soln. of tervalent molybdenum bromide, in an air-free flask, and conc. at 65°–70° under reduced press. until nearly dry. Alcohol was introduced, and the crystalline brick-red salt separated out. By a similar process an impure **rubidium molybdenum pentabromide** was obtained; and the double decomposition of the potassium salt and cæsium bromide furnishes **cæsium molybdenum pentabromide,** $Cs_2MoBr_5.H_2O$. They also prepared **potassium molybdenum hexabromide,** K_3MoBr_6, by adding 10 grms. of potassium bromide, in a sat. aq. soln., to 200 c.c. of a soln. of tervalent molybdenum bromide, and concentrating at 65°–70° under diminished press. to about 100 c.c. Air-free alcohol was then admitted to the flask, and the excess of potassium bromide precipitated. After filtration in an atmosphere of carbon dioxide, the filtrate was concentrated to 40 c.c. On addition of absolute alcohol a crystalline, light red solid was obtained which was filtered off and dried. All these soluble complex salts give deep red soln. with water, in which both potassium salts are very soluble, the rubidium salt is sparingly soluble, and the cæsium compound insoluble. The aq. soln. gradually turn brown, then turbid, and finally yield a dark brown precipitate. This decomposition is accelerated by warming. The salts reduce copper sulphate soln. to cuprous bromide, whilst silver nitrate soln. is reduced to the metal.

C. W. Blomstrand obtained a small yield of **molybdenum tetrabromide,** $MoBr_4$, as a product of the action of bromine on heated molybdenum. Molybdenyl dibromide sublimes first; green molybdenum tribromide appears near the hot zone, and most distant from the heated metal occur black needles of the tetrabromide. The exact conditions have not been established. The salt is fusible and volatile; it furnishes brownish-red vapour; it easily decomposes into the tribromide and bromine; it deliquesces rapidly in air to a black liquid; and it gives with water a yellowish-brown soln. from which alkalies precipitate hydrated molybdic oxide.

C. W. Blomstrand[3] found that a soln. of molybdous bromide in alkali-lye is gradually decomposed by air containing carbon dioxide forming golden-yellow crystals of **molybdenum dihydroxytetrabromide,** $Mo_3Br_4(OH)_2.8H_2O$; the crystals of the *octohydrate* were also produced by adding ammonium chloride to a hot, alkaline soln. of molybdous bromide; and by adding acetic acid to an alkali soln. of molybdous bromide. According to A. Atterberg, and C. W. Blomstrand, if the octohydrate be dried over sulphuric acid, it gives the dark red *dihydrate;* and if one of the hydrates be dried at 100° or in vacuo over sulphuric acid, a red powder of the anhydrous salt is formed. If it has not been heated over 90°, it dissolves completely in alkali-lye. The octohydrate forms a yellow, amorphous powder which rapidly loses water in air. If the hydrate be heated until all the water is expelled, and the residue treated with alkali-lye, a black powder—possibly molybdous oxide—remains. Hydrochloric acid dissolves the product; nitric acid attacks the salt; and, according to W. Muthmann and W. Nagel, it is decomposed by alkali hydroxide to form hydrated molybdic oxide. The alkaline soln. is precipitated by acids to form mixed salts, $[Mo_3Br_4]X_2.nH_2O$, as indicated above. Hydrogen sulphide was found by A. Atterberg to precipitate hydrated molybdic oxide; and A. Atterberg also studied the action of potassium cyanide.

According to A. Atterberg, an alkaline soln. of molybdenum dihydroxytetrabromide yields a dark reddish-yellow precipitate of **molybdenyl bromide,** $MoOBr,\frac{1}{2}H_2O$, when treated with ammonium molybdate and acetic acid; the colour becomes reddish-brown at 100°. W. Wardlaw and A. J. I. Harding prepared the bromide by precipitating a conc. soln. of a tervalent molybdenum bromide in acetone.

> 25 grms. of molybdenum trioxide and 350 c.c. of the hydrobromic acid were heated under a reflux condenser for 3 to 6 hours, when a golden-brown liquid was finally obtained. The filtered soln. was electrolyzed in a diaphragm cell with smooth platinum electrodes, a current of 3·5 amps. being used, until the cathode soln. was reddish-brown. This soln. was transferred to an air-free flask and conc. at 70° under diminished press. to 80–100 c.c. The liquid was then transferred to a small cell and re-electrolyzed to ensure that the molybdenum was tervalent. The electrolysis was continued until a sample of the liquid added to air-free acetone gave a flocculent fawn precipitate of molybdenyl bromide. (If the electrolysis is continued beyond this stage, the product is hydrolyzed and is much darker than the true compound.) The cathode soln. was now forced by press. of carbon dioxide into air-free acetone, and the solid which separated was filtered off and washed with acetone. All these operations were performed in an atm. of carbon dioxide, air being rigidly excluded. The solid was transferred to a desiccator which was then evacuated.

The composition is $MoOBr.4H_2O$. The dried solid is light fawn in colour and does not deliquesce in the air, although it gradually undergoes atm. oxidation. It is readily soluble in water or hydrobromic acid, its solubility in water being greater than that of the oxychloride. It is insoluble in acetone or dry ether, slightly soluble in cold absolute alcohol and more soluble on warming. The substance has pronounced reducing properties. Silver nitrate is reduced to the metal, whilst with lead acetate acidified with acetic acid no precipitate of lead bromide is obtained. This test seems to indicate that molybdenyl bromide is not a binary electrolyte. The mol. wts. determined by the depressions of the f.p. of soln. of 0·1235, and 0·0640 grm. in 10 grms. of air-free water are, respectively, 218·8 and 218·2. This agrees with the assumption that the salt is a co-ordination compound $[MoOBr.4H_2O]$, which undergoes gradual hydrolysis, $[MoOBr,4H_2O]+H_2O=[MoO.5H_2O]Br =[MoO.5H_2O]^{\cdot}+Br'$. This view receives support from the fact that the mol. wts. determined with soln. of the solid, after standing some hours in ice-cold water, were considerably less than those quoted above, whilst after longer periods the hydroxide of molybdenum gradually separated. The mol. conductivity of soln. of a mol of the salt in 24 litres of water at 1°, changes from 66·8 in 2 min. to 78·2 in 9 min. The rate of hydrolysis is faster in more dil. soln.

E. Weinland and W. Knöll found that when the product of the action of hydrogen bromide on heated molybdenum trioxide, is dissolved in warm, 40 per cent. hydrobromic acid until bromine is no longer evolved, and the soln. crystallized over sulphuric acid, green hygroscopic needles of **molybdenum hydroxytetrabromide,** $Mo(OH)Br_4.2H_2O$, are formed. They are rapidly decomposed in humid air. If the soln. used in the preparation of this salt be allowed to stand over soda-lime at 30°, dark brown, hygroscopic prisms of **molybdenum oxyhydroxydibromide,** or

molybdyl dibromide, $MoO(OH)Br_2.1\frac{1}{2}H_2O$, are formed. The aq. soln. is brown, and ammonia precipitates hydrated molybdenum pentoxide.

The **molybdenyl tribromide,** $MoOBr_3$, has not been isolated. A. Chilesotti observed that by the electrolytic reduction of molybdenum trioxide in hydrochloric or sulphuric acid soln. of suitable concentration, a soln. of quinquevalent molybdenum is formed if a platinized platinum cathode is employed, but with a polished platinum cathode, a tervalent salt is produced. The complex **ammonium molybdenyl pentabromide,** or **ammonium molybdenum oxypentabromide,** $2NH_4Br.MoOBr_3$, or $MoOBr_3(NH_4Br_2)(ONH_4)$, or $(NH_4)_2[MoOBr_5]$, was obtained by E. Weinland and W. Knöll, from a hydrobromic acid soln. of the components. It forms reddish-brown, octahedral crystals. F. G. Angell, R. G. James and W. Wardlaw prepared the ammonium salt by reducing electrolytically a soln. of molybdenum trioxide in hydrobromic acid to the quinquevalent state, and transferred the soln. in a current of nitrogen to an air-free flask containing a soln. of ammonium bromide. The light brown crystals were washed with hydrobromic acid of sp. gr. 1·7, drained, and dried in vacuo over potassium hydroxide and phosphorus pentoxide. The mother-liquor furnishes other crops when concentrated and seeded with crystals of the salt. According to E. Weinland and W. Knöll, an analogous process furnishes by using Mo : K in the proportions 2 : 1, **potassium molybdenyl pentabromide,** K_2MoOBr_5, in black or dark red crystals; similarly with **rubidium molybdenyl pentabromide,** Rb_2MoOBr_5, in dark red or green, rhombic pyramids; and **cæsium molybdenyl pentabromide,** Cs_2MoOBr_5, in garnet-red, octahedral crystals. F. G. Angell and co-workers obtained potassium molybdenum oxypentabromide, $K_2[MoOBr_5].2H_2O$, in dark brown needles; rubidium molybdenum oxypentabromide, $Rb_2[MoOBr_5]$, as a yellow solid; **pyridinium molybdenum oxypentabromide,** $(C_5H_6N)_2[MoOBr_5])$, in yellowish-green needles; and **quinolinium molybdenum oxypentabromide,** $(C_9H_8K_2[MoOBr_5]$, in golden-brown crystals. A. Rosenheim and M. Koss, and E. Weinland and W. Knöll also prepared the pyridine and quinoline complex salts. The calculated mol. wts., and those calculated from the depression of the f.p. of the salts, dissolved in air-free water, as well as the osmotic factor *i*, are, in aq. and alcoholic soln.,

		NH_4-	K_4-	Rb-	C_5H_6N-	C_9H_8N-salt.
Aq. Soln.	Calculated .	547·7	625·8	682·5	671·7	771·8
	v . . .	121–16·3	314–22·2	42·8	284–27·8	129–32
	By lowering f.p.	51·5–60·1	61·9–68·3	71·0	62·9–73·2	71·7–87·7
	i . . .	62·9–73·2	71·7–87·7	9·6	10·7–9·1	10·7–8·8
Alco. Soln.	*v* . . .	29·4–19·5	—	—	28·2–19·1	27·6–16·1
	By lowering .	29·4–19·5	—	—	219–214	179–264
	i . . .	3·84–4·12	—	—	3·07–3·14	431–2·92

The mol. electrical conductivities, μ, of soln. with *v* litres per mol, were:

$(NH_4)_2[MoOBr_5$	*v* . .	14·3	28·5	57·0	114·0	228·1	456·3
	μ . .	561·0	598·8	613·0	655·0	689·3	757·0
$K_2[MoOBr_5]$	*v* . .	19·7	39·4	78·9	157·8	315·5	631·0
	μ . .	450·1	487·1	515·2	526·8	566·1	660·4

and similarly with the pyridinium and quinolinium salts. The chlorides are green, and the bromides brown to yellow when dry, but in aq. soln. these salts are extensively hydrolyzed and ionized. By treatment with thiocyanic acid, they yield black thiocyanates, $R_2[MoO(CyS)_5]$, insoluble in water but readily soluble in alcohol. The bromides are more sensitive to oxidation than the chlorides. Like the chlorides, the complex bromides in absolute alcohol give an osmotic factor approximating $i=3$, and the soln. retain the characteristic colour of the salts themselves. This is taken to mean that in alcoholic soln., the formula of the salts are of the co-ordination type $R_2[MoOX_5]$, rather than $2RX.MoOX_3$, where the osmotic factor would be nearly $i=1$. An alcoholic soln. ionization is in accord with $R_2[MoOX_5]\rightleftharpoons 2R^{\cdot}+[MoOX_5]''$; and hydrolytic decomposition does not occur as is the case in aq. soln. where the colours are quite different from those in alcoholic soln. E. Weinland and W. Knöll prepared **magnesium molybdenyl pentabromide,** $Mg(MoOBr_5).7H_2O$, in hygroscopic, olive-green, octahedral crystals or six-sided pyramids.

E. Weinland and W. Knöll prepared **potassium molybdenyl tetrabromide,** or **potassium oxytetrabromide,** $KMoOBr_4.2H_2O$, or $K[MoOBr_4H_2O].H_2O$, in olive-green columnar columns, from a hydrobromic acid soln. of the component salts with Mo : K=1 : 4. F. G. Angell and co-workers doubt if the salt is olive-green because, whilst the oxytetrachlorides are green, the oyxtetrabromides they obtained are all red. They prepared red, hygroscopic crystals of **lithium molybdenum oxytetrabromide,** $Li[MoOBr_4(H_2O)].3H_2O$, from the electrolytically reduced soln. of quinquevalent molybdenum in hydrobromic acid, by the addition of lithium bromide, cooled in ice. The product was washed with hydrobromic acid of sp. gr. 1·7, and dried over sodium hydroxide and phosphorus pentoxide. The corresponding **pyridinium molybdenum oxytetrabromide,** $(C_5H_6N)[MoOBr_4]$, was also obtained in red, hygroscopic needles, and **quinolinium molybdenum oxytetrabromide,** $(C_9H_8N)[MoOBr_4]$, in orange, hygroscopic needles, which when dried change to pink. The f.p. of the aq. soln. gives an osmotic factor $i=9{\cdot}0$ to 7·7 or a mol. wt. 56·5 to 66·5—calculated for the trihydrate 510·7. This corresponds with complete decomposition in aq. soln. In alcoholic soln., the osmotic factor i is nearly 3 indicating a dissociation $2R[MoOBr_4]\rightleftharpoons R_2[MoOBr_5]+MoOBr_3$. The lithium salt was also prepared by E. Weinland and W. Knöll; and they also reported that **calcium molybdenum oxytetrabromide,** $CaMoOBr_4.7H_2O$, or $Ca[MoOBr_4(H_2O)].6H_2O$, furnishes red, four-sided plates.

E. F. Smith and V. Oberholtzer obtained **molybdenum trioxytetrabromide,** $Mo_2O_3Br_4$, along with the trihydroxytribromide by the action of hydrogen bromide on molybdenum trioxide. The colour of the salt resembles that of potassium permanganate; the tabular crystals which are slowly acted upon by purified air, but not by carbon dioxide; they dissolve in water with the development of heat, forming a colourless soln. which becomes blue on standing. E. F. Smith and V. Oberholtzer obtained **molybdenum trihydroxytribromide,** $Mo(OH)_3Br_3$, as indicated above. The brownish-yellow volatile liquid at a low temp., and under reduced press., yields yellow needles, which liquefy as soon as air is admitted. The aq. soln. is very pale yellow, almost colourless, and becomes deep yellow on standing, and in about 24 hrs. deposits blue molybdenum oxide.

C. W. Blomstrand prepared **molybdenum dioxydibromide,** MoO_2Br_2, by heating molybdenum dioxide in bromine vapour; and by melting molybdenum trioxide with boric or phosphoric acid, and heating the cold and powdered mass with potassium bromide: $MoO_3+B_2O_3+2KBr=2KBO_2+MoO_2Br_2$. The yellowish-red, tabular crystals deliquesce in air; and they form a colourless soln. with water. F. G. Angell and co-workers obtained **lithium molybdenum dioxydibromide,** $Li[MoO_2Br_2(H_2O)_2].4H_2O$, from an electrolytically reduced soln. of quinquevalent molybdenum mixed with lithium bromide, evaporated to a small volume, and cooled in ice. The salt was washed in hydrobromic acid of sp. gr. 1·7, and dried over sodium hydroxide and phosphorus pentoxide.

REFERENCES.

[1] C. W. Blomstrand, *Journ. prakt. Chem.*, (1), **77**. 89, 1859; (1), **82**. 436, 1861; A. Atterberg, *Några Bidrag till kännedomen om Molybdän*, Upsala, 16, 1872; *Bull. Soc. Chim.*, (2), **18**. 21, 1872; *Akad. Afhandl. Upsala*, 1, 1872; W. Muthmann and W. Nagel, *Ber.*, **31**. 2010, 1898; K. Lindner and H. Helwig, *Zeit. anorg. Chem.*, **142**. 180, 1925; K. Lindner, *ib.*, **162**. 203, 1927; W. Lederer, *Darstellung und Untersuchung reinen geschmolzen Molybdäns*, München, 1911; F. W. Bergstrom, *Journ. Amer. Chem. Soc.*, **47**. 2317, 1925.

[2] C. W. Blomstrand, *Journ. prakt. Chem.*, (1), **82**. 435, 1861; F. W. Bergstrom, *Journ. Amer. Chem. Soc.*, **47**. 2317, 1925; W. Wardlaw and A. J. I. Harding, *Journ. Chem. Soc.*, 1592, 1926; H. J. Braun, *Untersuchungen über das Molybdan*, Berlin, 1904; A. Rosenheim and H. J. Braun, *Zeit. anorg. Chem.*, **46**. 311, 1905; F. Förster and E. Fricke, *Zeit. angew. Chem.*, **36**. 458, 1923.

[3] C. W. Blomstrand, *Journ. prakt. Chem.*, (1), **77**. 89, 1859; (1), **82**. 436, 1861; W. Wardlaw and R. L. Wormell, *Journ. Chem. Soc.*, 1087, 1927; W. Wardlaw and A. J. I. Harding, *ib.*, 1592,

1926; F. G. Angell, R. G. James, and W. Wardlaw, *ib.*, 2578, 1929; A. Atterberg, *Några Bidrag till kännedomen om Molybdän*, Upsala, 16, 1872; *Bull. Soc. Chem.*, (2), **18**. 21, 1872; *Akad. Afhandl. Upsala*, 1, 1872; W. Muthmann and W. Nagel, *Ber.*, **31**. 2010, 1898; E. F. Smith and V. Oberholtzer, *Zeit. anorg. Chem.* **4**. 236, 1893; E. Weinland and W. Knöll, *ib.*, **44**. 81, 1905; A. Rosenheim and M. Koss, *ib.*, **49**. 148, 1906; A. Chilesotti, *Zeit. Elektrochem.*, **12**. 173, 1906.

§ 22. Molybdenum Iodides, and Mixed Halides

J. J. Berzelius[1] found that iodine does not act on red-hot molybdenum; and that a soln. of hydrated molybdic oxide in hydriodic acid, behaves like the soln. in hydrochloric acid. M. Guichard found that when dry molybdenum pentachloride is heated in a current of dry hydrogen iodide, iodine is liberated, and brown, amorphous **molybdenum diiodide,** or **molybdous iodide,** MoI_2, is formed. The sp. gr. is 4·3. Molybdous iodide is insoluble in water and alcohol. When heated in vacuo up to the m.p. of glass, it is not decomposed, but when heated in air, iodine is liberated and an oxide is formed which, at a higher temp., is converted into molybdenum trioxide. Hydrogen reduces the iodide at 500°, and the change is very rapid at an incipient red-heat. Chlorine decomposes it below 240°, and bromine behaves similarly. In oxygen at 350°, there is vigorous incandescence, with a liberation of iodine and formation of molybdenum trioxide. Sulphur readily converts the iodide into a black sulphide, but nitrogen is without action at the softening point of glass. Water decomposes it very slightly at the ordinary temp., and a little more rapidly at 700°, whilst in superheated steam, hydrogen is liberated as well as hydrogen iodide, probably as a result of the decomposition of the steam by an oxide, MoO, formed as the first product of the action of the steam on the iodide. Hydrogen sulphide converts the iodide into sulphide, and sulphuric and nitric acids oxidize it slowly in the cold and more rapidly on heating. Potash-lye acts on it slowly at ordinary temp.

J. J. Berzelius obtained a red soln. by dissolving molybdenum tetrahydroxide in hydriodic acid. When the soln. is evaporated in air, it forms red or brown crystals which are soluble in water, and give off hydrogen iodide when heated leaving a residue of molybdenum dioxide. M. Guichard obtained **molybdenum tetraiodide,** MoI_4, by the action of liquid hydrogen iodide, under press., on molybdenum tetrachloride. The black crystals change in air, and lose iodine at 100°. The salt cannot be obtained free from chlorides.

J. H. Gladstone[2] observed that when hydrofluoric acid is added to a green soln. of molybdous oxide in hydrochloric acid, a rich purple precipitate is produced, and this is succeeded by a white precipitate which is insoluble in an excess of hydrofluoric acid, but readily soluble in hydrochloric acid reproducing the green soln. The white substance was said to be a compound of molybdenum with both halogens. O. Ruff and F. Eisner condensed hydrogen fluoride over powdered molybdenum pentachloride cooled by a freezing mixture, and, after the mixture had stood for some time, distilled off the hydrogen fluoride. There remained **molybdenum fluochloride,** $Mo_3F_{10}Cl_5$, as a blue solid. A. Atterberg prepared **molybdenum difluotetrabromide,** $Mo_3Br_4F_2.3H_2O$, as a yellow powder, by the action of hydrofluoric acid on an alkaline soln. of molybdenum dihydroxytetrabromide.

A. Atterberg, and C. W. Blomstrand prepared **molybdenum dichlorotetrabromide,** $Mo_3Br_4Cl_2.3H_2O$, by adding an excess of hydrochloric acid to an alkaline soln. of molybdenum dihydroxytetrabromide. The yellow powder loses no water at 100°; and when treated with boiling water, forms the dihydroxytetrabromide. C. W. Blomstrand prepared **molybdenum tetrachlorodibromide,** $Mo_3Cl_4Br_2,3H_2O$, by allowing a soln. of molybdous chloride or molybdenum dihydroxytetrachloride to stand in hot hydrobromic acid for some time. The cold soln. deposits crystals of the *trihydrate* which are insoluble in water, and in dil. hydrochloric acid; with fuming nitric acid, hydrogen bromide is given off. If a warm aq. soln. is allowed to stand on a water-bath it deposits red prisms of the *hexahydrate*. It is soluble in water; and it can be recrystallized from its soln. in dil. hydrobromic acid. It is soluble in alcohol and ether. When water is added to the alcoholic soln., there is precipitated **molybdenum hydroxytetrachlorobromide,** $Mo_3(OH)BrCl_4.2H_2O$. C. W. Blomstrand also prepared **ammonium molybdenum tetrachlorotetrabromide,** $2NH_4Br.Mo_3Cl_4Br_2.2H_2O$, in yellowish-red crystals, by saturating a soln. of molybdous chloride with potassium chloride and adding ammonia and hydrobromic acid. The salt is decomposed by water; it can be recrystallized from dil. hydrobromic acid, and it dissolves without decomposition in alcohol. Similarly with the preparation of **potassium molybdenum tetrachlorotetrabromide,** $2KBr.(Mo_2Cl_4)Br_2.2H_2O$.

C. W. Blomstrand obtained **molybdenum tetrachlorodiiodide,** $Mo_3Cl_4I_2.3H_2O$, from a hot soln. of molybdous chloride or molybdenum dihydroxytetrachloride in hydriodic acid. The *trihydrate* separates as a scaly crystalline precipitate. The mother-liquor, when concentrated on a water-bath, deposits dark red prisms of the *hexahydrate.* The salt is decomposed by water; and with fuming nitric acid, iodine separates out. It behaves towards alcohol like the tetrachlorodibromide. Dark yellowish-red crystals of **ammonium molybdenum tetrachlorotetraiodide,** $2NH_4I.Mo_3Cl_4I_2.2H_2O$, are formed by a method analogous to that used for the tetrachlorotetrabromide. Similarly with the preparation of **potassium molybdenum tetrachlorotetraiodide,** $2KI.(Mo_3Cl_4)I_2.2H_2O$. A. Atterberg, and C. W. Blomstrand prepared a complex with **molybdenum tetrabromodiiodide,** namely, $Mo_3(OH)_2Br_4.2Mo_3Br_4I_2.8H_2O$, from an alkaline soln. of dihydroxytetrabromide saturated with hydriodic acid. These mixed salts were discussed by I. Koppel, and K. Lindner and co-workers. K. Lindner and H. Helwig obtained pyridine salts of some mixed acids, namely, $C_5H_5N.HMo_3Br_4Cl_3$; $C_5H_5N.HMo_3Br_4Cl_3.C_2H_5OH$; and $C_5H_5N.HMo_3Br_4Cl_3$.

REFERENCES.

[1] J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817; *Ann. Chim. Phys.*, (2), **17**. 5, 1921; *Pogg. Ann.*, **4**. 153, 1825; **6**. 331, 369, 1826; **7**. 261, 1826; M. Guichard, *Compt. Rend.*, **123**. 821, 1896; *Ann. Chim. Phys.*, (7), **23**. 439, 1901; *Recherches sur les oxydes, les sulfures et les iodures de molybdène*, Paris, 1900.

[2] O. Ruff and F. Eisner, *Ber.*, **40**. 2926, 1907; A. Atterberg, *Några Bidrag till kännedomen om Molybden*, Upsala, 16, 1872; *Bull. Soc. Chim.*, (2), **18**. 21, 1872; *Akad. Afhandl. Upsala*, 1, 1872; C. W. Blomstrand, *Journ. prakt. Chem.*, (1), **77**. 89, 1859; (1), **82**. 436, 1861; J. H. Gladstone, *Chem. News*, **2**. 99, 1860; *Phil. Trans.*, **145**. 208, 1855; I. Koppel. *Zeit. anorg. Chem.*, **77**. 289, 1912; K. Lindner, E. Haller and H. Helwig, *ib.*, **130**. 209, 1923; K. Lindner and H. Helwig, *ib.*, **142**. 180, 1925.

§ 23. Molybdenum Sulphides

M. Guichard[1] found that when molybdenum disulphide is heated in the electric arc-furnace for 2 to 4 min., a mixture of molybdenum and **molybdenum hemitrisulphide,** or **molybdic sulphide,** Mo_2S_3, is formed. The metal can be removed by treatment with cold dil. aqua regia. W. Muthmann and co-workers heated molybdenite mixed with calcium oxide and fluoride in the arc-furnace, and obtained bluish black crystals. M. Guichard found that this sulphide forms steel-grey needles of sp. gr. 5·9 at 15°, and it is rather harder than molybdenite. If heated in the electric arc-furnace, it forms molybdenum; and when heated in sulphur vapour, molybdenum disulphide is formed. M. Picon observed that this sulphide is largely dissociated at 1100°, and volatilization occurs at 1200°. W. Muthmann and co-workers found that this sulphide is not attacked by conc. hydrochloric acid. K. von der Heide studied the action of potassium cyanide on molybdic sulphide. V. Montoro found that the X-radiogram of the supposed sesquisulphide is the same as that of molybdenite, MoS_2, superposed on that of a molybdenum hemicarbide, MoC_2, and that the latter disappears after the substance has been treated with dil. aqua regia.

The history of **molybdenum disulphide,** MoS_2, and its occurrence as **molybdenite,** has been discussed in connection with the history, and occurrence of molybdenum. F. Cornu applied the term **jordiste** to the colloidal mineral from Himmelsfürst, Freiberg, which has the same composition as molybdenite. Analyses of molybdenite were made by C. F. Bucholz, R. Brandes, P. Jannasch, A. Cossa, L. F. Svanberg and H. Struve, W. Gerrie, A. Liversidge, H. Seybert, C. M. Wetherill, J. C. Ilsemann, J. C. H. Heyer, R. Nasini and E. Baschieri, K. Nenadkewitsch, and F. Zambonini. The results agree with the formula MoS_2, and with the analyses of L. F. Svanberg and H. Struve, and M. Guichard of the artificial compound. Molybdenum disulphide was prepared by C. W. Scheele, and J. J. Berzelius by heating one of the higher sulphides in a closed vessel; and by heating molybdenum trioxide admixed with sulphur, or in a current of hydrogen sulphide. M. Guichard heated a mixture of 150 grms. of potassium carbonate, 310 grms. of sulphur, and 200 grms. of molybdenum dioxide at a high temp. for half an hour, and washed out the potassium polysulphide by means of water. A. de Schulten used a similar process. M. Guichard obtained the same compound by heating a mixture of 50 grms. of ammonium molybdate, 100 grms. of sulphur, and some lamp-black. St. Meunier used a similar process. J. Milbauer found it to be a product of the action of potassium thiocyanate on molybdenum oxide at a high temp. C. W. C. Fuchs calcined a mixture of molybdenum trioxide and cinnabar; and H. Debray heated a mixture of ammonium molybdate and an excess of lime in a current of hydrogen chloride and sulphide; E. Péchard obtained it by the action of hydrogen sulphide on an acidic soln. of molybdenum dioxide; and C. Winssinger, by the action of an excess of dil. acetic acid on potassium sulphomolybdate. C. Winssinger found that if the product so obtained be dialyzed for about 72 hrs., a brown, neutral liquid—**colloidal molybdenum disulphide**—is formed. F. V. von Hahn prepared colloidal sols by the cathodic discharge. P. Bary and J. V. Rubio, and P. Bary studied the structure of the dried gel.

J. J. Berzelius described molybdenum disulphide as a black powder; and E. Péchard, as a reddish-brown precipitate, Molybdenite occurs in lead-grey masses which may be foliated, scaly, or granular. The crystals are hexagonal in form and appear in flexible but not elastic plates resembling mica, or in short prisms which are slightly tapering. The prismatic planes are horizontally striated; and striæ sometimes occur on the base normal to the edges. A. Knop said that thin plates are green. The cleavage of the crystals resembles that of mica, and thin sheets of the mineral several square centimetres in area may be scaled off from a large crystal of molybdenite. These sheets have a metallic lustre and look not unlike sheets of lead foil. They can be readily electroplated with copper, so that connecting wires may be soldered to them. The streak, said J. L. C. Schröder van der Kolk, is greenish-grey. H. Schneiderhöhn examined polished sections of the mineral. J. B. L. Romé de l'Isle compared the crystals of molybdenite with those of mica and talc. R. J. Haüy said that the *présumée forme primitive* is a rhombic prism. J. G. Schmeisser described the crystals as hexagonal prisms; J. F. L. Hausmann, as regular six-sided plates; and F. Mohs, as rhombohoidal (trigonal). N. A. E. von Nordenskjöld doubted if the crystals are hexagonal. M. Hörnes, and N. von Kokscharoff said that the crystals are monoclinic or possibly rhombic; and P. Groth, rhombic. G. A. Kenngott, however, showed that the crystals are probably hexagonal; and A. P. Brown gave for the axial ratio of the hexagonal crystals $a:c=1:1\cdot9077$. This is in agreement with the observations of A. J. Moses, W. E. Hidden, W. C. Brögger, and O. Mügge. A. J. Moses found that the corrosion figures of molybdenite agree with those for hexagonal crystals. R. G. Dickinson and L. Pauling found that the X-radiograms agreed with a typical, hexagonal, layer lattice. Each hexagonal unit contains two molecules of the disulphide, and has an axial ratio 1·95. Each sulphur atom is equidistant from three molybdenum atoms, and each molybdenum atom is surrounded by six equidistant sulphur atoms at the corners of a small triangular prism of altitude 3·17 A., and edge 3·15 A.—Fig. 28 when the circles represent sulphur atoms, and the black spots, molybdenum atoms. There is a layer of sulphur atoms each side of a layer of molybdenum atoms; two layers of sulphur atoms are in contact. The sulphur atoms form pyramids which are 3·66 A. in length along the pyramid edges, and 3·15 A. along the basal edges. The distance of the molybdenum atom to the nearest sulphur atom is 2·41 A. The excellent basal cleavage of molybdenite is connected with the relatively great distance between the sulphur atoms. A. E. van Arkel, J. W. Gruner, V. Montoro, and E. J. Cuy made some observations on this subject. O. Hassel studied the structure of the disulphide, and H. Mark, the deformation produced by stresses. F. Mohs found the sp. gr. of molybdenite to be 4·591 ; and H. Seybert, 4·444. M. Guichard gave 4·80 for the sp. gr. at 14° of the artificial crystals, and 4·88 at 14° for the amorphous disulphide. A. de Schulten gave 5·06 for the sp. gr. of the artificial crystals. The hardness of molybdenite is 1·0 to 1·5. Observations on this subject were made by A. Reis and L. Zimmermann. E. Jannettaz found the heat conductivity from a central point of the prisms furnished an ellipse with the axes 1 : 2 or 1 : 3. F. E. Neumann gave 0·1067 for the sp. ht. ; A. de la Rive and F. Marcet, 0·1097 ; and H. V. Regnault, 0·12334. H. V. Regnault observed that the disulphide is not altered by heating it to a high temp. out of contact with air. E. D. Clark said that when heated in the oxyhydrogen blowpipe flame, molybdenite fuses at once and forms a white sublimate containing minute globules of metal, and a molten mass of metal resembling arsenical iron. J. Joly gave 450° for the temp. of sublimation. R. Cusack gave 1185° for the m.p. ; and G. Spezia added that if heated in the oxyhydrogen flame, the disulphide melts and forms a white crystalline sublimate and a yellowish-white vapour. N. Parravano and G. Malquori found that for the dissociation of the disulphide log p_{S_2} is $-11·963$ at 600° ; $-7·620$ at 805° ; $-6·463$ at 910° ; $-5·453$ at 1005° ; and $-4·629$ at 1100°. M. Picon studied the thermal decomposition of the sulphide. A. W. Meyer found the index of refraction, μ ; the absorption coeff., k ; and the reflecting power, R, for light of wave-length $\lambda = m\mu$, to be for molybdenite :

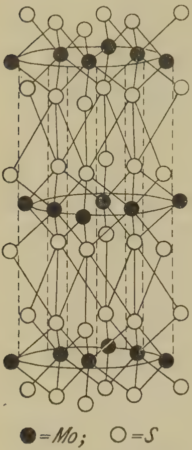


FIG. 28. — The Arrangement of Atoms in Molybdenite, MoS_2.

λ	500	450	410	370	350	330
μ	5·668	4·675	4·002	3·209	2·640	2·217
k	0·341	0·581	0·812	0·963	0·982	1·001
R	52·97	56·75	59·71	52·93	47·13	42·10

Observations on the optical constants were also made by E. P. T. Tyndall. A. de Gramont observed that the spark spectrum does not show the sulphur lines, but molybdenum lines are well-defined. A. Cossa said that the yellowish-green flame gives a continuous spectrum ; and a phosphate bead is blue in the reducing flame ; and a borax lead when heated in the oxidizing flame is yellow when hot and white when cold. W. W. Coblentz found that the ultra-red reflection spectrum of molybdenite is uniform—18 to 20 per cent.—through the spectrum up to 14μ. Molybdenite has four maxima of selective reflection in the ultra-violet at 260, 450, 610, and $690\mu\mu$ respectively. The ultra-red transmission spectrum shows that molybdenite is very opaque up to 15μ. I. B. Crandall found that molybdenite has a low transmission in the visible region followed by great transparency and high reflectivity in the ultra-red. A decrease in temp. to the b.p. of liquid air greatly increases the transparency of molybdenite. A sample transparent to $0·702\mu$ at room temp., was transparent to $0·666\mu$ at $-190°$. For incident light of wave-length 1μ, $2·2\mu$, and 4μ, W. W. Coblentz and C. W. Hughes found the percentage absorptions of the incident light in traversing 0·3 mm. layer were respectively 22·3, 18·1, and 18·1 ; the percentage light reflected at the first surface, 29·8, 27·8, and 27·8 ; the percentage sums of returning light, 39·0, 38·1, and 38·0 ; the percentage sums of the transmitted light, 40·5, 45·0, and 45·0 ; and the indices of refraction, respectively 3·40, 3·23, and 3·23. I. B. Crandall calculated the indices of refraction for light of wave-length λ to be :

λ . .	0·6757	0·6915	0·7136	0·80	3·0	5·0	7·0μ
μ . .	14·8	9·48	7·44	6·00	4·02	3·98	3·90

E. P. T. Tyndall found two maxima in the variation of the index of refraction in the visible spectrum at 600$m\mu$ and 660$\mu\mu$. There is also anomalous dispersion. O. Stelling studied the X-ray absorption spectrum.

R. G. Harvey measured the electrical conductivity. T. W. Case observed the change in the electrical resistance of molybdenite in light. S. L. Martin showed that the result is not a contact effect ; and W. W. Coblentz, that the change is more marked with natural than with artificial molybdenite ; and it is destroyed by heating to 700°. A photoelectric change occurs in the resistance of molybdenite when it is subject to an impressed e.m.f. and exposed to thermal radiation between λ=0·36μ in the ultra-violet to beyond λ=9μ in the ultra-red. W. W. Coblentz showed that the effect of increasing the intensity of the exciting radiations is to produce a more rapid response in the long wave-lengths than in the short wave-lengths, with a resultant shift of the spectral photoelectric sensitivity curve toward the long wave-lengths. There is no simple law governing the variation in the photoelectric response in molybdenite, with variation in intensity of the radiation stimulus. At room temp. there are maxima of sensitivity in the regions of λ=0·7μ, 0·85μ, 1·02μ, and 1·8μ. Beyond 2·5μ the photoelectric sensitivity is practically nil. Raising the temp. causes a rapid decrease in the spectral photoelectric sensitivity, especially in the regions of 1·02μ to 1·8μ. At 80° the spectral photoelectric sensitivity has practically disappeared—only slight indications being observed for radiations of wave-lengths λ=0·6μ to 0·8μ. The effect produced by lowering the temp. is greatly to increase the sensitivity curve throughout the whole spectrum from the ultra-violet to 2·5μ in the infra-red. This increase in sensitivity is greatest in the region of 0·8μ to 0·9μ, so that at the temp. of boiling liquid air the maximum sensitivity occurs at about 0·85μ, with a new band at 1·25μ to 1·35μ. Samples of molybdenite which are quite insensitive at room temp. become fairly sensitive, photoelectrically, at —178°. At low temp., the spectral photoelectric sensitivity curves of all samples are quite similar, with a maximum in the region of 0·8μ to 0·9μ. From this it would appear that this photoelectric property is one of degree rather than one of quality. The fact that the bands at 1·02μ and 1·8μ occur together, and that the 0·85μ band may occur alone suggests the possibility that they are characteristic bands of spectral photoelectric sensitivity of different sulphur compounds of molybdenum. Using frequency instead of wave-length to indicate the spectral position of the radiations which cause the maximum change in electrical conductivity, it is found that in some instances there is a constant difference of the wave numbers analogous to the series relations of spectral lines. The time required for recovery of equilibrium in electrical conductivity is close to twice the time of exposure. Mechanical working of the material appears to lower the photoelectric sensitivity. There appears to be no close connection between photoelectric sensitivity and current rectification in molybdenite. The greatest photoelectrical activity occurs in the region of the spectrum, where there is a rapid decrease in spectral absorption. While selenium is photopositive in that on exposure to light the electrical conductivity greatly increases, some samples of molybdenite are photonegative in that the resistance in light is greater than it is in darkness. W. W. Coblentz found that the two opposing effects may occur simultaneously. The photopositive reaction occurs quickly and prevails on low voltages. The photonegative action usually builds up more slowly and predominates on high voltage. It is selective to the wave-length of the radiation stimulus, as well as to the magnitude and direction for the electric current through the crystal. Temp. also affects the phenomenon, and under certain conditions, on exposure of the molybdenite, the photonegative reaction occurs first followed by the photopositive action. For the short wave-length region of the spectrum, extending to about 0·67μ, the photoelectric reaction in one sample of molybdenite passed from purely positive on low voltages through intermediate stages to an apparently purely negative reaction on high voltages. Furthermore, this reaction is dependent upon the direction of the current through the crystal. On high voltages a secondary negative reaction appears to be present. The recovery after exposure is also unusual. When operated on the intermediate voltages, on shutting off the radiation stimulus, the negative effect still further increases, after which the crystal gradually returns to its former dark conductivity. However, at moderately low temp., —20°, the recovery from the photonegative reaction is irregular, resulting in overshooting so that momentarily the apparent resistance is lower than the normal dark resistance. At a given temp. the region of transition in the spectrum, in which the action changes from photonegative to photopositive, is very narrow (less than 9 A.). It appears to shift slightly toward the short wave-lengths with decrease in temp. or increase in intensity of the radiation. The critical voltage is very small. Under certain temp. conditions an increase of 1 volt sufficed to change a small positive-negative galvanometer deflection of ± 1 cm. into a pure negative deflection of perhaps —25 cms. With decrease in temp. the potential must be increased in order to produce a negative reaction. S. L. Martin, and D. S. Steinberg also discussed the photoelectric effect.

Molybdenite not only shows a photoelectric change in resistance when subjected to an impressed e.m.f. and exposed to thermal radiation; but it shows an actinoelectric effect in that an e.m.f. may be manifested when it is exposed to thermal radiation without an impressed e.m.f. The actinoelectrical phenomenon is more common than is the photoelectric effect; occurring in both the high and the low resistance classes of molybdenite. The intrinsic sensitivity of the actinoelectric reaction seems to be the highest in the low-resistance class of molybdenite, which is just the opposite of the photoelectric reaction. Both effects are usually observed in small spots or loci in the lamina; and both phenomena may be found in the same lamina. The actinoelectric e.m.f. of these spots, which are sometimes separated by only 0·5 to 1·5 mm., may be positive or negative. The polarity of this e.m.f. does not appear to have any relation with the positive and negative thermal e.m.f. observed at the ends of the sample, connected with the copper electrodes. The spectral actinoelectric effect may be positive or negative, depending upon the wave-length of the thermal radiation stimulus, as is the case with the photoelectric effect. The maximum of the spectral actinoelectric reaction is produced by thermal radiation stimuli of wave-lengths between 0·65 and 0·9μ. There may be several such maxima in this spectral region. The material seems to be insensitive actinoelectrically to radiation stimuli of wave-lengths greater than about 1μ. On the other hand, the maxima of the spectral photoelectric reaction in molybdenite usually occur beyond 0·8μ; and the sensitivity extends to 2μ. Moreover, the magnitude of the photoelectrical reaction may be from 75 to 100 times greater than the actinoelectrical response. Hence, since the former is usually observed with an insensitive galvanometer the actinoelectrical reaction has no effect upon previously published data on the spectraphotoelectrical sensitivity of molybdenite. The time for attaining the maximum spectral actinoelectric response is practically instantaneous irrespective of the kind (high or low resistance) of molybdenite examined, and of the wave-length of the exciting radiation. On the other hand, in the typical, high-resistance, high-photoelectrical sensitivity class of molybdenite, for certain wave-lengths of the exciting radiation, the photoelectrical reaction requires from one to several minutes to attain a maximum, and twice that time for recovery after exposure to thermal radiation. In the typical low-resistance, low-photoelectrical sensitivity but high-actinoelectrical sensitivity class of molybdenite, the spectra-photoelectrical reaction appears to be instantaneous irrespective of the wave-length of the radiation stimulus. Lowering the temp. shifts the maximum of the actinoelectrical reaction toward the short wave-lengths; but this shift is much less than obtains in the photoelectric reaction. Lowering the temp. has no marked effect upon the intrinsic actinoelectric sensitivity, as compared with the marked increase in photoelectrical sensitivity observed under similar conditions. Increasing the intensity of the exciting radiation appears to produce a more rapid response on the short wave-length side than on the long wave-length side of the maximum of the spectral actinoelectric reaction, which is just the reverse of the previously observed, spectrophotoelectric reaction under similar conditions. A. Verneuil observed the effect of traces of molybdenite on the phosphorescence of calcium sulphide. J. O. Perrine found that the fluorescence of molybdenite is not excited by the X-rays.

H. F. Vieweg found that the frictional electricity developed by molybdenite is like that developed by sulphur. F. Beijerinck, and C. Doelter found that the electrical conductivity of molybdenite at ordinary temp. is very small. J. Königsberger and O. Reichenheim observed that as the temp. rises, the conductivity increases. The resistance taken in the direction of the *C*-axis was found to be :

	19·5°	73°	92·5°	400°	750°	1020°
R . .	29·0	17·24	15·0	3·9	1·14	0·751 ohm.

and perpendicular to *C*-axis :

	−185°	−145°	−65°	19°	64°	113°
R . .	750,000	13,000	306	29	10·5	6·18 ohm.

They found that molybdenite frequently contains inclusions of the mineral chlorite. C. Tubandt and M. Haedicke said that molybdenite conducts like a metal below 200°. M. J. Huizinga mentioned the presence of a dark blue liquid on the surface of a molybdenite detector ; W. W. Coblentz noticed that the liquid is exuded from some samples when an electric current is passed through them ; and A. T. Waterman, that oxidation is preceded by local eruptions of the dark blue liquid. W. W. Coblentz suggested that the liquid is the blue, colloidal molybdenum oxide described by M. Guichard. G. W. Pierce's values for the electrical resistance and conductivity of a sample of molybdenite are plotted in Fig. 30. J. Okubo, O. U. von Willer, G. Gottstein, and P. Collet also measured the resistance of molybdenite. F. Streintz found that the compressed powder of molybdenite is a good conductor. C. Tubandt and M. Haedicke found that compressed cylinders of molybdenum disulphide, between 200° and 300° behave like metallic conductors. A. T. Waterman showed that the resistance of molybdenite is very high with a small applied potential difference, but it diminishes rapidly with increasing potential difference. The effect is illustrated by Fig. 29. The effect is partly due to the rise in temp. caused by the electric current ; but this is probably a minor cause of the phenomenon. The diminution of resistance with increasing potential difference continues uniformly up to a certain potential difference, which varies to some extent with different specimens and according to the treatment to which they have been subjected : at this point, which will be referred to as " the break," the resistance diminishes

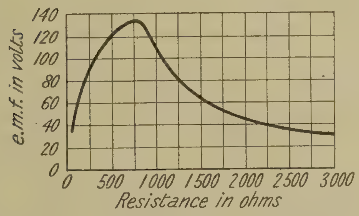


FIG. 29.—The Effect of an Applied Electromotive Force on the Resistance of Molybdenite.

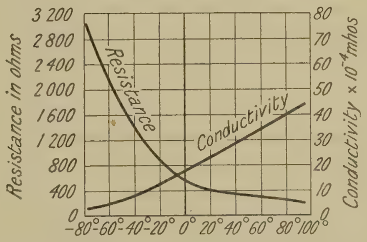


FIG. 30.—Electrical Resistance and Conductivity of Molybdenite.

suddenly and the mineral conducts, at a red-heat, with a comparatively low resistance. Before the voltage has been raised sufficiently for the break to occur the resistance diminishes, as has been noted above, with increasing voltage, whereas after the break the resistance diminishes with diminishing voltage. This difference may be regarded as characteristic of two stages, α and β, of the material which occur before and after the break. The phenomenon of the break is reversible, but the rate of change of state decreases after long heating. The substance also tends to persist in the state in which it was when the current was turned off. The light sensitivity becomes inappreciable as the conductivity of molybdenite becomes metallic. Heating the mineral to redness in a Bunsen flame for several minutes reduced the resistance to $\frac{1}{2}$ or $\frac{1}{4}$ its value, but further heating produced practically no further effect. The resistance was diminished to about half value by the momentary passage of a high voltage discharge, as from a small induction coil, but repetition caused no further decrease. The resistance is not affected by strong magnetic fields. J. Königsberger investigated the relation between the electrical conductivity and the light-absorption of the crystals; and P. H. Geiger found that if molybdenite be connected in a closed circuit with a galvanometer, and one surface of contact be illuminated, a photoelectric current is generated. J. Weiss and J. Königsberger found that the thermoelectric force of the copper-molybdenite couple is $7{\cdot}27\times10^{-4}$ volt per degree of temp. between 20° and 80°; $7{\cdot}60\times10^{-4}$ volt between 68·7° and 57·0°; and $7{\cdot}46\times10^{-4}$ volt between 57·0° and 45·8°. The current flows from the hot junction to the copper. G. W. Pierce found the thermoelectric force of different samples of molybdenite against copper at 20° varied from 110 to 175 and from —230 to —750 millivolts; and against lead, from 113 to 178 and from —227 to —717 millivolts. With the cold junction zero, the e.m.f. with a copper-molybdenite couple was —7·5 millivolts with the hot junction at 10·1°, and —130·0 millivolts at 195°. The intermediate values varied linearly with temp. O. U. von Willer observed an e.m.f. of 560 microvolts by passing a current from copper to molybdenite to copper, and the temp. of the junctions differed by one degree. In the thermoelectric couple the current flowed from copper to molybdenite at the hot junction. W. Ogawa, and M. Kimura and co-workers studied the thermoelectric properties of molybdenite.

G. Gottstein measured the Hall effect, and the Ettinghausen effect. G. Gottstein found a relatively large difference in the adiabatic and the isothermal Hall effects of molybdenite, but C. W. Heaps found the difference much smaller.

C. W. Heaps found that there is a decrease in the resistance of molybdenite in a magnetic field, and the result is little affected by the direction of the field. According to I. Bernfeld, in the electrolysis with electrodes of metallic sulphides, the following changes occur. (1) In acid soln.: at the anode, the metal is dissolved and the sulphur precipitated or oxidized; at the cathode, hydrogen sulphide is formed with separation of the metal; (2) in alkaline soln.: at the anode, the metal forms a hydroxide, and the sulphur is oxidized; at the cathode, the metal is precipitated and the sulphur passes into soln. as an ion. In electrolyzing molybdenum disulphide in fused potassium hydroxide, E. F. Smith found that the sulphur is oxidized to sulphate. W. W. Coblentz, and G. W. Pierce discussed the rectifying action of molybdenite. H. S. Roberts and L. H. Adams, M. J. Huizinga, and E. T. Wherry found molybdenite to be a fair radio-detector.

H. Rose found that the disulphide is not decomposed by hydrogen at a red-heat; but O. F. von der Pfordten observed that if strongly heated in hydrogen, the disulphide is reduced to molybdenum. N. Parravano and G. Malquori showed that in the reaction $MoS_2+2H_2\rightleftharpoons 2H_2S+Mo$, $\log K=\log (P_{H_2S}/P_{H_2})$, and

	805°	910°	1005°	1100°
$\log (P_{H_2S}/P_{H_2})$ . . .	—2·235	—2·059	—1·863	—1·319
Q	77,400	79,200	80,000	81,100 cals.

According to J. J. Berzelius, when molybdenum disulphide is heated in air, it forms molybdenum trioxide and sulphide ; and, as indicated above, A. T. Waterman found that the oxidation of molybdenite is preceded by local eruptions of a dark blue liquid. P. H. A. de Clermont and J. Frommel showed that the disulphide is not decomposed by water, but H. V. Regnault said that it is decomposed by steam at a red-heat. C. W. Blomstrand observed that molybdenite is easily attacked by chlorine, but not so readily by bromine ; and A. Cossa added that when heated in chlorine, the disulphide is completely converted into pentachloride. M. Guichard said that sulphur vapour, at ordinary press., does not transform the disulphide into trisulphide. E. F. Smith found that the vapour of sulphur monochloride at 300° partially decomposes the disulphide. Boiling sulphuric acid, said J. J. Berzelius, forms sulphur dioxide and a blue soln ; the cold acid has very little action. Warm aqua regia converts it into molybdic and sulphuric acids ; and nitric acid oxidizes it easily. According to H. B. North and C. B. Conover, molybdenite is not attacked by thionyl chloride at 150° to 175°. If mixed with potassium nitrate and detonated, potassium molybdate is formed. P. Camboulives found that the vapour of carbon tetrachloride converts any oxide in molybdenite into molybdenum chloride. E. Péchard found that the disulphide is soluble in a soln. of potassium cyanide ; and K. von der Heide studied this reaction. P. Berthier found that it is decomposed when heated to redness with lead oxide. A. Cossa found that molybdenite acquires a film of gold when immersed in a soln. of gold chloride ; and in copper sulphate soln. in contact with a strip of zinc, it slowly acquires a film of copper.

According to F. Mawroff and M. Nikoloff,[2] **molybdenum pentasulphide,** Mo_2S_5, is obtained as a *trihydrate*, $Mo_2S_5.3H_2O$, by reducing with zinc a soln. of ammonium molybdate, containing more than 20 per cent. of sulphuric acid, until the colour is dark red, and then diluting, filtering, and saturating with hydrogen sulphide. The precipitate is collected and washed with hot water and then with alcohol. It is then shaken repeatedly with carbon disulphide, washed with ether, and dried at 68°–75°. One mol. of water is lost at 135°–140°, but further heating causes decomposition. The hydrated sulphide dissolves in warm soln. of alkali sulphides to give bright red soln. depositing an orange precipitate on cooling. It dissolves with difficulty, but completely, in warm conc. hydrochloric acid. Careful heating in carbon dioxide gives the anhydrous sulphide, Mo_2S_5, which is almost black. When the hydrated compound is heated in hydrogen sulphide, an exchange of water for hydrogen sulphide takes place, and the *hemitrisulphohydrate*, $2Mo_2S_5.3H_2S$, is formed.

J. J. Berzelius[3] prepared **molybdenum trisulphide,** MoS_3, by saturating a soln. of an alkali molybdate with hydrogen sulphide, or by dissolving molybdenum trioxide in a soln. of an alkali sulphide or ammonium sulphide, and decomposing the sulphomolybdate so formed by dil. hydrochloric or sulphuric acid. The reddish-brown, gelatinous precipitate becomes dark brown when dried. The precipitate may contain some admixed sulphur or molybdic acid. A. Atterberg said that when precipitated from cold soln., the precipitate is more slimy, more easily oxidized, and less easily washed than when obtained from hot soln. R. F. Weinland and F. Sommer found that in order to get a trisulphide of a high degree of purity it is necessary to start from a pure sulphomolybdate. The precipitation of molybdenum as trisulphide, by passing hydrogen sulphide into a cold, acid soln. of molybdic acid, is incomplete, heat is necessary ; and if the soln., sat. with hydrogen sulphide, is heated in a closed vessel for a long time at 100°, the molybdenum is precipitated quantitatively as trisulphide provided the right proportion of acid be present in the soln. This subject was discussed above in connection with the analytical reactions of molybdenum. J. Milbauer found that the trisulphide is the one produced by the action of potassium thiocyanate on molybdenum oxide at a high temp. L. Moser and M. Behr, E. Wendehorst, and by L. Dede and T. Becker obtained the compound in this manner. J. J. Berzelius observed that the molybdenum trisulphide may appear as a colloidal soln., for he said that the sulphide is somewhat soluble in water, particularly hot water, forming a dark yellow soln., and this is probably the peptized trisulphide. C. Winssinger studied the properties of colloidal molybdenum trisulphide. J. J. Berzelius showed that when heated to a high temp., the trisulphide passes into the disulphide. G. Preuner and I. Brockmöller measured the vap. press. of sulphur, p mm., from the trisulphide for temp. between 450° and 500°, and N. Parravano and G. Malquori, between 390° and 450° :

	355°	390°	418°	450°	475°	480°	500°
p . . .	40	28·8	178·6	(80)	250	313	980

M. Wasjuchnowa gave 34 mm. at 450° ; 195 mm. at 475° ; 255 mm. at 480° ; and 560 mm. at 500° ; while E. T. Allen and R. H. Lombard gave 31 mm. at 450° and 170 mm. at 475°. According to O. F. von der Pfordten, the trisulphide is reduced to metal when heated to a high temp. in hydrogen. As shown by E. Collett and M. Eckardt, when the sulphide is roasted to transform it into trioxide, there is a tendency for small particles to be projected violently from the crucible, and also a tendency for some of the oxide to be lost by volatilization. The trisulphide, said J. J. Berzelius, dissolves in conc. soln. of potassium hydroxide partially as oxysulphomolybdate. F. Feigl, and O. Ruff and B. Hirsch discussed the association of sulphur with the trisulphide, $MoS_3.S_n$, where the sulphur is not removed by camphor bromide. Molybdenum trisulphide unites with basic metal sulphides to form sulphomolybdates, $R_2'MoS_4$—*vide infra.*

J. J. Berzelius[4] stated that molybdenum forms not only di- and tri-sulphides, but also **molybdenum tetrasulphide,** MoS_4, which he prepared as follows :

A soln. of potassium paramolybdate is sat. with hydrogen sulphide and the nearly black liquid is boiled for some hours in a retort to drive off hydrogen sulphide. The cold soln. is filtered, and the black powder of molybdenum disulphide is separated from the heavier scaly crystals of a compound of the tetrasulphide and potassium sulphide, as well as possible, by levigation. The salt of the tetrasulphide is collected on a filter, and washed with cold water until the washings no longer give a blackish-brown, but rather a red, precipitate with hydrochloric acid. The red scaly crystals on the filter are treated with boiling water which leaves insoluble red molybdenum disulphide, and a dark red soln. The soln. is treated with an excess of hydrochloric acid, and the precipitated molybdenum tetrasulphide washed with water.

G. Krüss prepared the tetrasulphide by melting molybdic acid with potassium carbonate, extracting the melt with water, and passing hydrogen sulphide into the soln. when heated to the b.p. A black powder together with a crystalline substance separates out. This mixed material is washed first with cold water, then with hot water to dissolve out the molybdenum di- and tri-sulphides, and the resultant chocolate-brown powder is heated in a current of hydrogen sulphide until its weight is constant. J. J. Berzelius said that the tetrasulphide, when freshly prepared, is dark red, and translucent; it shrinks considerably when dried, forming a grey, granular mass which is cinnamon-brown when ground up to powder with water. G. Krüss said that the powder is very hygroscopic ; J. J. Berzelius added that it is not decomposed by water or by acids. According to G. Krüss, when the tetrasulphide is oxidized by chlorine or bromine in alkaline soln., alkali sulphate and molybdate are formed. Boiling sulphuric acid forms a reddish-yellow liquid which deposits sulphur and emits sulphur dioxide. For the observation of F. Feigl, and of O. Ruff and B. Hirsch, *vide supra.* Soln. of alkali sulphides dissolve the tetrasulphide, forming sulphomolybdates, $R_2'MoS_5$.

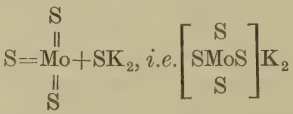
REFERENCES.

[1] C. W. Scheele, *Akad. Handl. Stockholm*, 247, 1778 ; J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817 ; *Ann. Chim. Phys.*, (2), **17**. 5, 1921 ; *Pogg. Ann.*, **4**. 153, 1825 ; **6**. 331, 369, 1826 ; **7**. 261, 1826 ; J. O. Perrine, *ib.*, (2), **22**. 48, 1923 ; T. W. Case, *ib.*, (2), **9**. 305, 1917 ; K. von der Heide, *Ueber Verbindungen niederen Molybdänoxyde und -sulfide mit Ammoniak und Cyankalium,* München, 1897 ; C. W. Heaps, *Phil. Mag.*, (6), **24**. 813, 1912 ; (7), **6**. 1283, 1928 ; G. Gottstein, *Ann. Physik*, (4), **43**. 1079, 1914 ; *Ueber die Prüfung thermodynamischer und elektronentheoretischer Formeln an Halbleitern,* Freiburg i. Br., 1913 ; E. T. Wherry, *Amer. Min.*, **10**. 28,

1925; H. S. Roberts and L. H. Adams, *ib.*, **7**. 136, 1922; C. Tubandt and M. Haedicke, *Zeit. anorg. Chem.*, **160**. 297, 1927; J. Milbauer, *ib.*, **42**. 433, 1904; H. Mark, *Zeit. Kryst.*, **61**. 75, 1924; O. Hassel, *ib.*, **61**. 92, 1924; M. J. Huizinga, *Proc. Acad. Amsterdam*, **19**. 512, 1917; O. U. von Willer, *Proc. Roy. Soc. N.S.W.*, **55**. 220, 1921; S. L. Martin, *ib.*, **58**. 150, 1924; A. E. van Arkel, *Physica*, **4**. 286, 1924; H. F. Vieweg, *Journ. Phys. Chem.*, **30**. 865, 1926; A. Reis and L. Zimmermann, *Zeit. phys. Chem.*, **102**. 298, 1922; M. Guichard, *Recherches sur les oxydes, les sulfures et les iodures de molybdène*, Paris, 1900; *Ann. Chim. Phys.*, (7), **23**. 439, 1901; *Compt. Rend.*, **129**. 1239, 1899; **130**. 137, 1900; E. Péchard, *ib.*, **118**. 804, 1894; P. Collet, *ib.*, **158**. 1994, 1914; P. Camboulives, *ib.*, **150**. 221, 1910; A. Verneuil, *ib.*, **103**. 600, 1886; *Bull. Soc. Chim.*, (2), **46**. 302, 1886; C. Winssinger, *Bull. Acad. Belg.*, (3), **15**. 390, 1888; G. Cesaro, *ib.*, 115, 1904; P. Berthier, *Ann. Chim. Phys.*, (2), **39**. 251, 1828; P. H. A. de Clermont and J. Frommel, *ib.*, (5), **18**. 189, 1879; H. V. Regnault, *ib.*, (2), **62**. 385, 1836; J. Okubo, *Science Rep. Tohoku Univ.*, **12**. 299, 1924; W. Muthmann, L. Weiss and A. Mai, *Liebig's Ann.*, **355**. 111, 1907; A. de Gramont, *Compt. Rend.*, **118**. 591, 746, 1894; *Analyse spectrale directe des minéraux*, Paris, 1895; *Bull. Soc. Min.*, **18**. 274, 1895; E. Jannettaz, *ib.*, **15**. 136, 1892; A. de Schulten, *ib.*, **12**. 545, 1889; *Geol. För. Förh. Stockholm*, **11**. 401, 1889; F. Streintz, *Ann. Physik*, (4), **9**. 854, 1902; I. Bernfeld, *Zeit. phys. Chem.*, **25**. 46, 1898; O. Stelling, *ib.*, **117**. 175, 1925; *Zeit. Physik*, **50**. 506, 1928; O. F. von der Pfordten, *Ber.*, **17**. 731, 1885; E. F. Smith, *ib.*, **23**. 2276, 1890; *Chem. News*, **62**. 206, 1890; *Journ. Franklin Inst.*, **127**. 313, 1889; **130**. 145, 1891; *Journ. Amer. Chem. Soc.*, **20**. 289, 1898; O. Mügge, *Neues Jahrb. Min.*, i, 109, 1898; A. Knop, *ib.*, 46. 1858; A. T. Waterman, *Phil. Mag.*, (6), **33**. 225, 1917; *Phys. Rev.*, (2), **21**. 388, 540, 1923; I. B. Crandall, *ib.*, (2), **2**. 343, 1913; E. P. T. Tyndall, *ib.*, (2), **21**. 162, 1923; G. W. Pierce, *ib.*, (1), **28**. 153, 1909; F. Beijerinck, *Neues Jahrb. Min. B.B.*, **11**. 428, 1897; W. C. Brögger, *Zeit. Kryst.*, **10**. 507, 1885; **16**. 5, 1890; F. Zambonini, *ib.*, **40**. 211, 1905; V. Goldschmidt, *ib.*, **21**. 330, 1893; H. Debray, *ib.*, **46**. 1102, 1858; M. Hörnes, *Ber. Mitt. Freund. Naturwiss.*, **2**. 253, 1847; J. D. Dana, *A System of Mineralogy*, New York, 33, 1868; 41, 1892; W. E. Hidden, *Amer. Journ. Science*, (3), **32**. 204, 1886; A. J. Moses, *ib.*, (4), **17**. 359, 1904; H. Seybert, *ib.*, (1), **4**. 320, 1822; C. M. Wetherill, *ib.*, (2), **15**. 443, 1853; G. A. Kenngott, *Uebersicht der Resultate mineralogischer Forschungen*, Wien, 105, 1855; C. W. C. Fuchs, *Die künstlich dargestellten Mineralien nach Roses System geordnet*, Haarlem, 57, 1872; V. Montoro, *Atti Accad. Lincei*, (6), **9**. 331, 1929; M. Picon, *Compt. Rend.*, **189**. 96, 1929; R. G. Harvey, *Econ. Geol.*, **23**. 778, 1928; W. Ogawa, *Journ. Japan. Soc. Chem. Ind.*, **31**. 476, 1928; J. W. Gruner, *Amer. Min.*, **14**. 173, 470, 1929; J. B. L. Romé de l'Isle, *Cristallographie*, Paris, **2**. 500, 1783; R. J. Haüy, *Traité de Minéralogie*, Paris, **4**. 290, 1801; J. F. L. Hausmann, *Handbuch der Mineralogie*, Göttingen, 197, 1813; F. Mohs, *Grundriss der Mineralogie*, Dresden, 576, 1824; N. von Kokscharoff, *Materialien zur Mineralogie Russlands*, St. Petersburg, **2**. 267, 351, 1857; N. A. E. von Nordenskjöld, *Beskrifning öfver de i Finland funna Mineralier*, Helsingfors, 19, 1855; P. Groth, *Tabellarische Uebersicht der Mineralien*, Braunschweig, 18, 1898; *Die Mineraliensammlung der Kaiser Wilhelms Universität Strassburg*, Strassburg, 23, 1878; P. Jannasch, *Journ. prakt. Chem.*, (2), **45**. 37, 1892; L. F. Svanberg and H. Struve, *ib.*, (1), **44**. 257, 1848; *Svenska Akad. Handl.*, 75, 1848; *Phil. Mag.*, (3), **33**. 409, 524, 1848; G. Spezia, *Atti Accad. Torino*, **22**. 419, 1887; C. Doelter, *Sitzber. Akad. Wien*, **109**. 49, 1910; A. Liversidge, *Proc. Roy. Soc. N.S.W.*, **29**. 316, 1895; K. Nenadkewitsch, *Trav. Musée Géol. Pierre le Grand*, St. Petersburg, **1**. 81, 1907; **5**. 37, 1911; R. Nasini and E. Baschieri, *Atti Accad. Lincei*, (5), **21**. 692, 1912; A. Cossa, *ib.*, (3), **1**. 206, 1877; *Gazz. Chim. Ital.*, **7**. 505, 1877; W. W. Coblentz, *Science Papers Bur. Standards*, **18**. 585, 1922; **19**. 375, 1924; *Journ. Washington Acad.*, **12**. 411, 1922; *Journ. Amer. Opt. Sur.*, **4**. 249, 1920; **7**. 63, 1923; *Phys. Rev.*, (2), **21**. 714, 1923; (2), **29**. 615, 1927; *Positive and Negative Photoelectrical Properties of Molybdenite and Several other Substances*, Washington, 1920; *Supplementary Investigations of Infra-red Spectra*, Washington, 1908; *Some New Thermoelectrical and Actinoelectrical Properties of Molybdenite*, Washington, 1924; *Various Photoelectrical Investigations*, Washington, 1922; W. W. Coblentz and C. W. Hughes, *Ultraviolet Reflecting Power of Some Metals and Sulphides*, Washington, 1924; W. W. Coblentz and H. Kahler, *Some Optical and Photoelectrical Properties of Molybdenite*, Washington, 1919; *Journ. Washington Acad.*, **9**. 537, 1919; W. W. Coblentz, M. B. Long and H. Kahler, *Phys. Rev.*, (2), **18**. 497, 1918; P. H. Geiger, *ib.*, (2), **22**. 461, 1923; A. W. Meyer, *Phys. Rev.*, (2), **27**. 247, 1926; *Journ. Amer. Opt. Soc.*, **13**. 557, 1926; A. P. Brown, *Proc. Acad. Philadelphia*, 210, 1896; R. G. Dickinson, *Journ. Amer. Chem. Soc.*, **44**. 276, 1922; R. G. Dickinson and L. Pauling, *ib.*, **45**. 1466, 1923; E. J. Cuy, *ib.*, **49**. 201, 1927; F. Cornu, *Koll. Zeit.*, **4**. 190, 1909; F. V. von Hahn, *ib.*, **36**. 277, 1925; R. Cusack, *Proc. Roy. Irish Acad.*, (3), **4**. 399, 1897; J. L. C. Schröder van der Kolk, *Centr. Min.*, 78, 1901; J. Königsberger, *ib.*, 601, 1908; *Phys. Zeit.*, **4**. 495, 1903; J. Königsberger and O. Reichenheim, *Centr. Min.*, 454, 1905; *Neues Jahrb. Min.*, ii, 22, 1906; O. Reichenheim, *Ueber die Elektrizitätsleitung einiger natürlich-kristallisierter Oxyde und Sulfide und des Graphits*, Freiberg i. Br., 1906; J. Weiss and J. Königsberger, *Phys. Zeit.*, **10**. 956, 1909; R. Gans, *Ann. Physik*, (4), **20**. 293, 1906; P. Bary, *Rev. Gén. Colloides*, **6**. 209, 1928; P. Barry and J. V. Rubio, *Compt. Rend.*, **189**. 294, 1929; F. E. Neumann, *Pogg. Ann.*, **13**. 1, 1831; H. Rose, *ib.*, **75**. 319, 1848; A. de la Rive and F. Marcet, *ib.*, **52**. 120, 1841; *Bibl. Univ.*, **28**. 360, 1840; *Ann. Chim. Phys.*, (2), **75**. 113, 1840; H. Schneiderhöhn, *Anleitung zur mikroskopischen Bestimmung und Untersuchungen von Erzen und Aufbereitungsprodukten besonders in auffallenden Licht*, Berlin, 1922; M. Kimura, K. Yamamoto and R. Ich'inote, *Mem. Coll. Eng. Kyoto*, **2**. 59, 1910; E. D. Clark, *The Gas Blowpipe*, London, 78, 1819; St. Meunier, *La Nature*, **36**. 32, 1890; J. C. Ilsemann, *Crell's Ann.*, i, 407, 1787; J. C. H. Heyer, *ib.*, ii, 124, 1787;

§ 24. Sulphomolybdates and Oxysulphomolybdates

As indicated in connection with molybdenum trisulphide, J. J. Berzelius[1] prepared a series of sulphomolybdates, $R_2'MoS_4$, by the union of a mol of a basic metal sulphide with a mol of molybdenum trisulphide. A mol of the basic sulphide may also unite with two or three mols of molybdenum sulphide forming respectively $R_2'Mo_2S_7$, and $R_2'Mo_3S_{10}$. The soluble sulphomolybdates are prepared by the action of hydrogen sulphide on soln. of the molybdates; or by the action of the soluble sulphides on molybdenum trisulphide. The insoluble sulphomolybdates are formed by adding a soln. of the alkali or alkaline earth sulphomolybdate to a soln. of the metal salt. A. Werner represented the formation of the sulphomolybdate, $K_2[MoS_4]$, by the equation:



$$\mathrm{S{=}}\overset{\overset{\textstyle \mathrm{S}}{\|}}{\underset{\underset{\textstyle \mathrm{S}}{\|}}{\mathrm{Mo}}}+\mathrm{SK_2},\ i.e.\left[\begin{matrix}\mathrm{S}\\ \mathrm{SMoS}\\ \mathrm{S}\end{matrix}\right]\mathrm{K_2}$$

J. J. Berzelius prepared **ammonium sulphomolybdate,** $(NH_4)_2MoS_4$, by evaporating a soln. of ammonium molybdate sat. with hydrogen sulphide; by evaporating a soln. of molybdic acid in ammonium sulphide; by dissolving freshly precipitated molybdenum trisulphide in ammonium sulphide, and adding alcohol, or evaporating the liquid. G. Krüss dissolved 5 grms. of ammonium paramolybdate in 15 c.c. of water, added 50 c.c. of aq. ammonia of sp. gr. 0·94, passed hydrogen sulphide into the liquid which became yellow, and then deep red, and, in about half an hour, the liquid deposited blood-red, tabular crystals with a green shimmer. According to C. von Haushofer, the rhombic bipyramids have the axial ratio $a : b : c = 0{\cdot}7846 : 1 : 0{\cdot}5692$. From J. W. Retgers', and H. Vater's observations, the sulphomolybdates and sulphotungstates are isomorphous. G. Krüss said that the crystals become matt and dark violet in air; and J. J. Berzelius said dark brown. They decompose at 100° losing some ammonium sulphide. The crystals are freely soluble in water, and sparingly soluble in alcohol. There is a loss of ammonium sulphide when the aq. soln. is evaporated. According to R. Fernandes, ammonium sulphomolybdate is stable in an atm. of ammonia; but

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C. F. Bucholz, *Scherer's Journ.*, **9**. 485, 1902; *Gehlen's Journ.*, **4**. 603, 1807; *Phil. Mag.*, **16**. 193, 1803; *Nicholson's Journ.*, **20**. 121, 188, 253, 1808; *Journ. Mines*, **18**. 241, 1808; R. Brandes, *Schweigger's Journ.*, **29**. 325, 1820; F. von Kobell, *Tafeln zur Bestimmung der Mineralien*, München, 25, 1894; J. G. Schmeisser, *A System of Mineralogy*, London, **2**. 258, 1794; D. S. Steinberg, *Journ. Russ. Phys. Chem. Soc.*, **56**. 572, 1924; J. Joly, *Phil. Mag.*, (6), **27**. 1, 1914; N. Parravano and G. Malquori, *Atti Accad. Lincei*, (6), **7**. 109, 1928; *Gazz. Chim. Ital.*, **58**. 283, 1928; W. Gerrie, *Univ. Toronto Geol. Studies*, 24, 1927; C. W. Blomstrand, *Journ. prakt. Chem.*, (1), **77**. 89, 1859; (1), **82**. 436, 1861; H. B. North and C. B. Conover, *Journ. Amer. Chem. Soc.*, **37**. 2486, 1915; *Amer. Journ. Science*, (4), **40**. 640, 1916; M. Picon, *Bull. Soc. Chim.*, (4), **45**. 907, 1928; *Compt. Rend.*, **189**. 96, 1929.

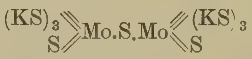
[2] F. Mawroff and M. Nikoloff, *Zeit. anorg. Chem.*, **95**. 188, 1916.

[3] J. J. Berzelius, *Svenska Akad. Handl.*, 125, 300, 1825; *Pogg. Ann.*, **7**. 262, 1826; *Ann. Chim. Phys.*, (2), **29**. 369, 1825; J. Milbauer, *Zeit. anorg. Chem.*, **42**. 433, 1904; F. Feigl, *Zeit. anal. Chem.*, **65**. 25, 1924; R. F. Weinland and K. Sommer, *Zeit. anorg. Chem.*, **15**. 42, 1897; O. Ruff and B. Hirsch, *ib.*, **151**. 81, 1926; L. Moser and M. Behr, *ib.*, **134**. 49, 1924; E. Wendehorst, *ib.*, **144**. 319, 1925; L. Dede and T. Becker, *ib.*, **152**. 185, 1926; C. Winssinger, *Bull. Acad. Belg.*, (3), **15**. 390, 1888; *Bull. Soc. Chim.*, (2), **49**. 452, 1888; O. F. von der Pfordten, *Ber.*, **17**. 731, 1885; A. Atterberg, *Några Bidrag till kännedomen om Molybdän*, Upsala, 16, 1872; *Bull. Soc. Chim.*, (2), **18**. 21, 1872; *Akad. Afhandl. Upsala*, 1, 1872; E. Collett and M. Eckardt, *Chem. Ztg.*, **33**. 968, 1909; M. Wasjuchnowa, *Ueber Gleichgewicht Cupri- Cuprosulfid*, Berlin, 1909; G. Preuner and I. Brockmöller, *Zeit. phys. Chem.*, **81**. 151, 1913; E. T. Allen and R. H. Lombard, *Amer. Journ. Science*, (4), **43**. 175, 1917; N. Parravano and G. Malquori, *Atti Accad. Lincei*, (6), **7**. 19, 1928.

[4] J. J. Berzelius, *Svenska Akad. Handl.*, 125, 300, 1825; *Pogg. Ann.*, **7**. 262, 1826; *Ann. Chim. Phys.*, (2), **29**. 369, 1825; G. Krüss, *Ueber die Schwefelverbindungen des Molybdäns*, Giessen, 1884; *Liebig's Ann.*, **225**. 1, 1884; *Ber.*, **16**. 2044, 1883; **17**. 1769, 1884; F. Feigl, *Zeit. anal. Chem.*, **65**. 25, 1924; O. Ruff and B. Hirsch, *Zeit. anorg. Chem.*, **151**. 81, 1926.

when it is exposed to air, it gives off ammonia and becomes dark green, dark violet, and finally black; and it absorbs water. If washed at this stage, it forms a dark red, microcrystalline **ammonium parasulphomolybdate,** $(NH_4)_5H_5[H_2(MoS_4)_6].10H_2O$, which is stable in air, and in a soln. of ammonium sulphomolybdate, but is decomposed by boiling water into ammonia, hydrogen sulphide, and molybdenum trisulphide. The formation of the parasulphomolybdate is represented by the equation: $6(NH_4)_2MoS_4=7NH_3+(NH_4)_5H_5[H_2(MoS_4)_6]$. It is also formed by saturating with hydrogen sulphide an ice-cold, conc. soln. of ammonium sulphomolybdate, or by keeping a warm aq. soln. of ammonium sulphomolybdate for several days. When a conc. soln. of ammonium sulphomolybdate is heated for 4 to 5 hrs. on a water-bath, a maroon-coloured, microcrystalline precipitate of **ammonium trisulphomolybdate,** $(NH_4)_4H_6[H_2(MoS_4)_6].16H_2O$, separates. The *guanidine sulphomolybdate*, Gu_2MoS_4, was obtained in dark red crystals; and also *guanidine parasulphomolybdate*, $Gu_5H_5[H_2(MoS_4)_6].8H_2O$, in dark red crystals. These sulphomolybdates are relatively stable; are not very soluble in water; and are decomposed when boiled with water. Hydrogen sulphide is evolved when the salts are treated with acids. It is supposed that these salts are derivatives of a hypothetical acid, $6H_2S=H_{10}[H_2S_6]$.

J. J. Berzelius prepared **lithium sulphomolybdate,** $Li_2MoS_4.nH_2O$, as an amorphous dark red mass by evaporating an aq. soln. of the components. It also forms a complex with more than one mol. of molybdenum trisulphide. Dark red crystals of **sodium sulphomolybdate,** Na_2MoS_4, were similarly prepared, as well as of **sodium sulphodimolybdate,** $Na_2Mo_2S_7.nH_2O$. R. Fernandes could not prepare *sodium trisulphomolybdate*, $Na_4H_6[H_2(MoS_4)_6]$, analogous to the ammonium salt. J. J. Berzelius prepared **potassium sulphomolybdate,** K_2MoS_4, by heating to bright redness a mixture of molybdenum disulphide, potassium carbonate, sulphur, and a little powdered charcoal; extracting the cold mass with water; evaporating the aq. soln.; and purifying the product by adding alcohol to the aq. soln. The salt is also formed by digesting molybdenite with a soln. of potassium pentasulphide; and by evaporating a soln. of potassium molybdate, saturated with hydrogen sulphide. G. Krüss obtained it by saturating with hydrogen sulphide a soln. of 5 grms. of potassium molybdate in 10 c.c. of water and 50 c.c. of potash-lye of sp. gr. 1·44 to 1·48, and allowing the soln. to stand some time for crystallization. C. F. Rammelsberg said that the rhombic bipyramids have the axial ratios $a:b:c=0·7651:1:0·5721$. C. von Haushofer said that the dark red crystals are isomorphous with those of the ammonium salt. According to J. J. Berzelius, when heated out of contact with air the salt becomes grey; about one-third remains undecomposed at a white-heat, and the remainder forms a mixture of potassium sulphide and molybdenum disulphide. G. Krüss and H. Solereder found that hydrogen reduces the salt to a mixture of potassium sulphide and molybdenum. J. J. Berzelius found that the salt is soluble in water forming a yellowish-red soln. from which alcohol precipitates the salt as a cinnabar red powder which then forms scaly crystals. If the aq. soln. of the sulphomolybdates are boiled in closed vessels, they deposit molybdenum disulphide and a complex with the tetrasulphide (*q.v.*) giving off at the same time hydrogen sulphide. The conc. aq. soln. are fairly stable in air, provided an excess of molybdenum trisulphide is present; but if the alkali sulphide predominates, or if free alkali be present, or if the soln. is dil., the soln. gradually darkens forming a compound with an excess of molybdenum trisulphide. This compound slowly decomposes with the separation of molybdenum trisulphide, and the supernatant liquor contains compounds of the alkali with sulphur acids, with molybdic acid, and with the blue oxide of molybdenum. Acids added to the aq. soln. precipitate molybdenum trisulphide with the liberation of hydrogen sulphide. Metal oxides which readily part with their oxygen form in the aq. soln. an alkali molybdate and a metal sulphide which enters into combination with the undecomposed molybdenum trisulphide. J. J. Berzelius prepared **potassium sulphodimolybdate,** $K_2Mo_2S_7$, as a dark grey substance, on adding a mineral acid, or preferably acetic acid, to an aq. soln. of the normal sulphomolybdate, and evaporating the brown liquid. The brown powder dissolves slowly in cold water, and rapidly in boiling water. The aq. soln. with an aluminium salt liberates hydrogen sulphide and precipitates molybdenum trisulphide and aluminium hydroxide; and similarly also with titanium salts. R. Fernandes prepared **potassium parasulphomolybdate,** $K_5H_5[H_2(MoS_4)_6].16H_2O$; but he could not obtain *potassium trisulphomolybdate,* $K_4H_6[H_2(MoS_4)_6]$, analogous to the corresponding ammonium salt. G. Krüss obtained crystals of **potassium orthosulphodimolybdate,** $3K_2S.2MoS_3$,



$$\begin{matrix}(KS)_3\\ S\end{matrix}\!>\!Mo.S.Mo\!<\!\begin{matrix}(KS)_3\\ S\end{matrix}$$

from a soln. of 5 grms. of potassium molybdate in 10 c.c. of water and 60 c.c. of potash-lye, of sp. gr. 1·53–1·56, sat. with hydrogen sulphide, by allowing it to stand for crystallization. The orange-red plates were thought by C. von Haushofer to be rhombic. They decompose after some time to form the normal sulphomolybdate. The salt is freely soluble in water, but insoluble in alcohol and ether. The aq. soln. decomposes slowly in air, and it gives a pale lemon-yellow precipitate with a barium salt; brownish-yellow with a manganous salt; olive-green with a cadmium salt; and dark brown with a uranyl salt. G. Krüss prepared **cæsium sulphomolybdate,** Cs_2MoS_4, in red needles.

J. J. Berzelius obtained **cupric sulphomolybdate,** $CuMoS_4$, as a dark brown precipitate; **silver sulphomolybdate,** Ag_2MoS_4, as a black precipitate; and **gold sulphomolybdate,** $Au_2(MoS_4)_3$, as a black powder. By boiling barium disulphide with water and an excess of molybdenum trisulphide, and cooling the filtered soln., J. J. Berzelius obtained **barium sulphotrimolybdate,** $BaS.3MoS_3$, in brownish-red crystals. The salt is easily attacked by dil. hydrochloric acid, but not by the conc. acid, precipitating molybdenum trisulphide. The evaporation of the mother-liquor gives **barium sulphomolybdate,** $BaMoS_4$. G. Krüss obtained **barium orthosulphodimolybdate,** $3BaS.2MoS_3$, from the potassium salt as indicated above. J. J. Berzelius obtained, as in the case of the corresponding barium salts, **strontium sulphotrimolybdate,** $SrS.3MoS_3$; **strontium sulphomolybdate,** $SrMoS_4$; **calcium sulphotrimolybdate,** $CaS.3MoS_3$; **calcium sulphomolybdate,** $CaMoS_4$; **beryllium sulphomolybdate,** $BeS.3MoS_3$; and **magnesium sulphotrimolybdate,** $MgS.3MoS_3$. F. Rodolico obtained a complex with hexamethylene tetramine, X, $MgMoS_4(X).10H_2O$. J. J. Berzelius prepared **zinc sulphomolybdate,** $ZnMoS_4$; and **cadmium sulphomolybdate,** $CdMoS_4$. G. Krüss also obtained **cadmium orthodisulphomolybdate,** $3CdS.2MoS_3$, from the potassium salt as indicated above. J. J. Berzelius prepared **mercurous sulphomolybdate,** Hg_2MoS_4, as a brownish-black precipitate; and **mercuric sulphomolybdate,** $HgMoS_4$, as a pale brown precipitate. J. J. Berzelius did not obtain **aluminium sulphomolybdate,** because the precipitate was hydrolyzed to aluminium hydroxide; but he obtained a soln. of **yttrium sulphomolybdate,** which precipitated yttrium hydroxide in a few hours. A black precipitate of **stannous sulphomolybdate,** and a brown precipitate of **stannic sulphomolybdate** were obtained; likewise also with **lead sulphomolybdate.**

For the **arsenic sulphomolybdates,** *vide* the sulpharsenates. J. J. Berzelius obtained **bismuth sulphomolybdate,** $Bi_2(MoS_4)_3$, as a dark brown precipitate.

L. Fernandes prepared some complex **sulphomolybdatovanadates** or **sulphovanadatomolybdates** with guanidine, Gu, thallium, and ammonium. Thus, **ammonium sulphovanadatomolybdate,** $(NH_4)_3H_5[H_2(MoS_4)_4(VS_3)_2].10H_2O$; $(NH_4)_5H_2[H_2(MoS_4)_3(VS_3)_3].12H_2O$; $(NH_4)_5H[H_2(MoS_4)_2(VS_3)_2].25H_2O$; **thallium sulphovanadatomolybdate,** $Tl_5H[H_2(MoS_4)_2(VS_3)_4].60H_2O$; and also **guanidine sulphovanadatomolybdate,** $Gu_5H_3[H_2(MoS_4)_4(VS_3)_2].15H_2O$; $Tl_5H_2[H_2(MoS_4)_3(VS_3)_3].22H_2O$; and $Tl_5H[H_2(MoS_4)_2(VS_3)_2].15H_2O$. J. J. Berzelius prepared **chromic sulphomolybdate,** as a dark brown precipitate; **uranyl sulphomolybdate,** as a dark brown precipitate; and G. Krüss obtained a dark brown uranyl salt corresponding with $3K_2S.2MoS_3$. J. J. Berzelius obtained **manganous sulphomolybdate** as a brownish-yellow precipitate, and a polysulphomolybdate as a dark red powder; and G. Krüss obtained a brownish-yellow magnanese salt corresponding with $3K_2S.2MoS_3$. J. J. Berzelius prepared **ferrous sulphomolybdate** as a rust-yellow powder; **ferric sulphomolybdate,** as a dark brown powder; **cobalt sulphomolybdate,** as a brownish-black precipitate; **nickel sulphomolybdate,** as a dark brown precipitate; and **platinum sulphomolybdate,** as a brownish-black precipitate.

In the course of the preparation of molybdenum tetrasulphide, G. Krüss obtained a blood-red liquid which furnished crystals of the composition $KHMoS_5$. When a soln. of this salt is treated with dil. hydrochloric or, better, acetic acid, **permonosulphomolybdic acid**, H_2MoS_5, is precipitated. This is washed successively with cold air-free water, alcohol, ether, carbon disulphide, and water-free ether, and dried in vacuo over sulphuric acid. The product loses hydrogen sulphide when warmed in a closed vessel, and at 140°, it passes into molybdenum tetrasulphide. It is insoluble in water, alcohol, ether, and acetic acid; with boiling conc. hydrochloric acid, hydrogen sulphide is evolved; hot, conc. sulphuric acid forms a reddish-yellow liquid which deposits sulphur and gives off sulphur dioxide; it forms a yellow liquid with warm alkali-lye; potassium hydrosulphide forms $KHMoS_5$; and potassium sulphide, K_2MoS_5. Many of the **permonosulphomolybdates,** $R_2'MoS_5$, reported by J. J. Berzelius may be oxysulphomolybdates.

J. J. Berzelius prepared **ammonium permonosulphomolybdate,** $(NH_4)_2MoS_5$, by digesting moist molybdenum tetrasulphide in a soln. of ammonium sulphide containing an excess of ammonia which lowers the solubility of the salt. The yellow powder becomes dark red when dried in air presumably owing to the loss of ammonium sulphide. The salt is sparingly soluble in cold water; freely soluble in hot water; and insoluble in aq. ammonia. J. J. Berzelius obtained **lithium permonosulphomolybdate,** Li_2MoS_5, as a pale yellow crystalline powder; **sodium permonosulphomolybdate,** Na_2MoS_5, as a reddish-yellow powder; and **potassium permonosulphomolybdate,** K_2MoS_5, by the method indicated in connection with molybdenum tetrasulphide, and also by the action of a soln. of potassium sulphide on moist molybdenum tetrasulphide. The ruby-red plates or powder decrepitate when heated; and they are decomposed into potassium trisulphide and molybdenum disulphide. The salt is sparingly soluble in cold water, but more soluble in boiling water. The hot soln. is red and does not give a precipitate on cooling; with hydrochloric acid, the aq. soln. gives a precipitate of molybdenum tetrasulphide. The salt is insoluble in cold potash-lye. According to G. Krüss, the salt obtained in the preparation of molybdenum tetrasulphide (*q.v.*), and considered by J. J. Berzelius to be K_2MoS_5, is really **potassium hydropermonosulphomolybdate,** $KHMoS_5$. It is also formed by the action of a soln. of potassium hydrosulphide on molybdenum tetrasulphide. The blood-red, rhombic prisms are quickly decomposed by moist air. Most metal salt soln. give red precipitates with the soln. of the potassium salt. K. A. Hofmann's analysis of a salt made by mixing NH_4MoS_3 with a soln. of potassium hydrosulphide agreed with the formula $KMoS_5$.

J. J. Berzelius prepared **copper permonosulphomolybdate,** $CuMoS_5$, as a dark red precipitate; dark brown **silver permonosulphomolybdate,** Ag_2MoS_5; dark brown **gold permonosulphomolybdate,** $Au_2(MoS_5)_3$; yellowish-red **barium permonosulphomolybdate,** $BaMoS_5$; scarlet-red **calcium permonosulphomolybdate,** $CaMoS_5$; red **magnesium permonosulphomolybdate,** $MgMoS_5$; red **zinc permonosulphomolybdate,** $ZnMoS_5$; red **cadmium permonosulphomolybdate,** $CdMoS_5$; reddish-brown **mercurous permonosulphomolybdate,** Hg_2MoS_5; red **mercuric permonosulphomolybdate,** $HgMoS_5$; dark brown **stannous permonosulphomolybdate;** red **stannic permonosulphomolybdate;** dark red **lead permonosulphomolybdate;** reddish-brown **bismuth permonosulphomolybdate;** dark red **chromic permonosulphomolybdate;** dark red **uranyl permonosulphomolybdate;**

red **manganese permonosulphomolybdate**; red **ferrous permonosulphomolybdate**; red **ferric permonosulphomolybdate**; reddish-brown **cobalt permonosulphomolybdate**; dark brown **nickel permonosulphomolybdate**; and dark red **platinum permonosulphomolybdate.**

According to K. A. Hofmann, when a soln. of ammonium sulphomolybdate is mixed with ammonium polysulphide, and allowed to remain 24 hrs., black needles of **ammonium perdisulphomolybdate,** $NH_4MoS_6.H_2O$, are formed, and more of the salt is precipitated by adding alcohol to the mother-liquor. The salt is purified by washing it successively with water, alcohol, ether, and carbon disulphide, and drying it over potassium hydroxide. It is sparingly soluble in water, and in alcohol. When treated with cold, 10 per cent. hydrochloric acid, **perdisulphomolybdic acid,** $HMoS_6$, is deposited. It is washed with carbon disulphide. If the ammonium salt is treated with a 10 per cent. soln. of potassium hydroxide for 24 hrs. at ordinary temp., dark brown leaflets of **potassium perdisulphomolybdate,** $KMoS_6$, are formed. The potassium salt is more soluble than the ammonium salt. Black insoluble prisms of **cæsium perdisulphomolybdate,** $CsMoS_6$, are similarly obtained; and likewise black, insoluble prisms of **thallium perdisulphomolybdate,** $TlMoS_6$.

F. Rodolico[2] prepared **magnesium oxytrisulphomolybdate** in association with hexamethylenetetramine, $MgMoS_3O.2X.10H_2O$. According to H. ter Meulen, if sodium sulphide acts on molybdenum oxychloride in absolute alcohol **molybdenum dioxysulphide,** MoO_2S, is formed. H. Debray prepared golden-yellow needles of **ammonium dioxydisulphomolybdate,** $(NH_4)_2MoO_2S_2$, by treating a conc. soln. of ammonium molybdate with ammonium sulphide at a low temp. L. Bodenstab obtained it by saturating with hydrogen sulphide a strong ammoniacal soln. of ammonium molybdate containing much ammonium chloride. The red prisms were washed with aq. ammonia and dried over sulphuric acid. G. Krüss obtained golden-yellow, monoclinic needles of the salt by passing hydrogen sulphide into a soln. of 5 grms. of ammonium paramolybdate in 15 c.c. of water and 25 c.c. of ammonia of sp. gr. 0·96, at 6°. The crystals which separate in about a quarter of an hour are washed with cold water, then with alcohol, and dried in vacuo. The yellow crystals redden on exposure to air. G. Krüss and H. Solereder reduced the salt to molybdenum by heating it in hydrogen. G. Krüss found that the salt is soluble in water; sparingly soluble in alcohol; and insoluble in ether and carbon disulphide. L. Bodenstab added that the crystals are sparingly soluble in cold water, and freely soluble in boiling water; insoluble in alcohol, and in a sat. soln. of ammonium chloride. The aq. soln. decomposes when boiled. Dil. hydrochloric acid precipitates molybdenum trisulphide from the aq. soln. without giving off hydrogen sulphide: $3(NH_4)_2MoO_2S_2+6HCl=2MoS_3+MoO_3+6NH_4Cl+3H_2O$. According to H. ter Meulen, if acetic acid is used in place of hydrochloric to decompose the dithiomolybdate, stable colloidal soln. of the trisulphide are obtained. The fusion of sodium carbonate and the trisulphide or tetrathiomolybdate also yields the dithiocompounds, $MoS_3+2Na_2CO_3=Na_2MoO_2S_2+Na_2S+2CO_2$. Cold, conc. sulphuric acid dissolves the salt, the soln. gradually darkens in colour, and the brownish-yellow soln. becomes green. Precipitates are produced by salts of the elements of the ammonium sulphide or hydrogen sulphide groups. L. Fernandes and F. Palazzo prepared polyphenolic, and pyridine complexes. G. Krüss prepared **potassium dioxydisulphomolybdate,** $K_2MoO_2S_2$, in reddish-yellow needles. F. Rodolico prepared **magnesium dioxydisulphomolybdate** in association with hexamethylenetetramine, $MgMoS_2O_2.2X.10H_2O$.

L. Fernandes and F. Palazzo regarded the oxysulphides of molybdenum as isopolyacids in which oxygen is partly replaced by sulphur. They prepared **sulphotrimolybdates** containing four substituted hydrogen atoms by strong acidification; and **oxysulphoparamolybdates** with five substituted hydrogen atoms by weak acidification. Ammonium salts with five substituted hydrogen atoms, and containing the group MoS_2O_2 could not be prepared, because, with the smallest addition of acid, tri-salts with four ammonium radicles were formed. Salts were prepared by adding increasing proportions of ammonium sulphomolybdate, $(NH_4)_2MoS_4$, to ammonium dioxydisulphomolybdate, $(NH_4)_2MoS_2O_2$, so as to obtain soln. with progressively increasing proportions of sulphur. Thus, $(NH_4)_4H_6[H_2(MoS_2O_2)_6].5H_2O$ was obtained as an orange-yellow powder, stable in air, by adding 1 to 15 c.c. of *N*-acetic acid to 10 grms. of ammonium dioxydisulphomolybdate dissolved in the smallest proportion of water, and washing the precipitate with alcohol and ether. If *N*-acetic acid be added to a soln. of equal parts of ammonium sulphomolybdate and dioxydisulphomolybdate, $(NH_4)_5H_5[H_2(MoS_3O)_3(MoS_2O_2)_3].16H_2O$ is formed as a maroon-red powder. The addition of *N*-acetic acid to soln. with proportions of ammonium sulphomolybdate, and dioxydisulphomolybdate in proportions up to 9 : 1, furnishes $(NH_4)_5H_5[H_2(MoS_3O)_6].27H_2O$.

By adding a soln. of guanidine acetate to a hot, dil. soln. of ammonium dioxydisulphomolybdate, and cooling, $Gu_4H_6[H_2(MoS_2O_2)_6].8H_2O$ is formed as an orange-yellow powder; if relatively dil. soln. be allowed to stand for some days, fire-red crystals of $Gu_5H_5[H_2(MoS_2O_2)_6].9H_2O$ appear; if acetic acid be added to soln. of guanidine acetate, and ammonium sulphomolybdate and dioxydisulphomolybdate, a maroon-red powder of $Gu_4H_6[H_2(MoS_2O_2)_3(MoS_3O)_3].10H_2O$ is formed; if only a very small proportion of acetic acid is used, red crystals of $Gu_5O_5[H_2(MoS_2O_2)_3(MoS_3O)_3].9H_2O$ are formed; and if the proportion of sulphomolybdate to dioxydisulphomolybdate is greater, dark red crystals of $Gu_5H_5[H_2(MoS_2O_2)_2(MoS_3O)_4].7H_2O$ are formed.

G. Krüss obtained **sodium trioxysulphomolybdate,** Na_2MoO_3S, by treating sodium trimolybdate with freshly prepared sodium hydrosulphide at 20°–30°, adding alcohol, and allowing the reddish-yellow oily precipitate to crystallize. The golden-yellow crystals are washed successively with alcohol, ether, carbon disulphide, ether, and alcohol, and dried in an air-bath at 100°. The hygroscopic crystals are freely soluble in water; acetic acid forms a green soln.; conc. sulphuric acid a deep blue soln. which becomes green. Ammonium sulphide transforms the salt into sodium sulphomolybdate. The soln. gives a yellowish-green precipitate with copper salts; a yellowish-white precipitate with zinc salts; and a yellow precipitate with barium salts. F. Rodolico prepared **magnesium trioxybisulphomolybdate** in association with hexamethylenetetramine, $MgMoSO_3.2X.10H_2O$.

G. Krüss prepared **ammonium hydrotetroxytrisulphodimolybdate,** $(NH_4)HMo_2O_4S_3$, by treating a soln. of ammonium paramolybdate, at about 90°, with ammonium hydrosulphide; and adding ammonium chloride to the cold soln. The reddish-yellow precipitate thus coagulates and it can be washed successively with water, alcohol, and carbon disulphide, and dried at 40°. It is also formed when a soln. of ammonium molybdate is sat. with hydrogen sulphide. The brownish-yellow product decomposes when heated in air; it develops hydrogen sulphide when boiled with water; it is soluble in water, but insoluble in alcohol, ether, and carbon disulphide. Hot, dil. soda-lye forms a reddish-yellow soln. which on cooling gives a precipitate of the sodium salt; potash-lye gives only a trace of the potassium salt. Hot, conc. alkali-lye precipitates sulphur, and olive-green molybdenum dioxide; with ammonia: $(NH_4)HMoO_4S_3+NH_3=(NH_4)_2MoO_2S_2+MoO_2S$; and with an excess of ammonium sulphide: $(NH_4)HMo_2O_4S_3+5(NH_4)_2S=2(NH_4)_2MoS_4+7NH_3+4H_2O$. Conc. nitric acid oxidizes the salt vigorously; and hot, conc. sulphuric acid forms a yellow liquid which gives off sulphur dioxide. G. Krüss prepared pale yellow, amorphous **sodium hydrotetroxytrisulphodimolybdate,** $NaHMo_2O_4S_3$, and lemon-yellow **potassium hydrotetroxytrisulphodimolybdate,** $KHMo_2O_4S_3$, in a similar manner. These salts can be regarded as derivatives of $2H_2Mo_2O_2S_2$ less a mol. of H_2S. Soln. of the alkali salts give brown or reddish-brown precipitates with soln. of salts of aluminium, chromium, manganese, copper, lead, silver, and uranium; and yellow precipitates with mercury, platinum, lanthanum, and cæsium salts.

G. Krüss found that if potassium trimolybdate be dissolved in a soln. of potassium hydrosulphide, and alcohol be added, a red oil is precipitated from which golden-yellow, monoclinic prisms of **potassium heptoxyenneasulphotetramolybdate,**

$K_8Mo_4O_7S_9$, can be separated. They are washed successively with alcohol, ether, and carbon disulphide, and dried at 100°. The golden-yellow, aq. soln. reddens when treated with acetic acid; and when the aq. soln. is heated to boiling molybdenum trisulphide is precipitated. When treated with a barium salt a yellow precipitate is formed at once, while with the normal sulphomolybdate the precipitate forms in 12 hrs., and with the sulphodiamolybdate, in a few minutes. Copper and lead salts give reddish-brown precipitates.

For **molybdenum enneachloroctosulphide,** $Mo_5S_8Cl_9$, *vide supra,* action of sulphur monochloride on molybdenum; and for $MoCl_5.N_4S_4$, *vide supra,* molybdenum pentachloride.

REFERENCES.

[1] J. J. Berzelius, *Svenska Akad. Handl.*, 125, 300, 1825; *Pogg. Ann.*, **7**. 262, 1826; *Ann. Chim. Phys.*, (2), **29**. 369, 1825; G. Krüss, *Ueber die Schwefelverbindungen des Molybdäns*, Giessen, 1884; *Liebig's Ann.*, **225**. 1, 1884; *Ber.*, **16**. 2044, 1883; **17**. 1769, 1884; G. Krüss and H. Solereder, *ib.*, **19**. 2729, 1886; J. W. Retgers, *Zeit. phys. Chem.*, **10**. 529, 1892; C. von Haushofer, *Zeit. Kryst.*, **8**. 379, 1884; H. Vater, *ib.*, **10**. 392, 1885; K. A. Hofmann, *Zeit. anorg. Chem.*, **12**. 55, 1896; A. Werner, *ib.*, **9**. 403, 1895; C. F. Rammelsberg, *Handbuch der krystallographisch-physikalischen Chemie*, **1**. 608, 1881; R. Fernandes, *Atti Accad. Lincei*, (6), **6**. 165, 1927; (6), **7**. 496, 1928; F. Rodolico, *ib.*, (6), **7**. 660, 1928.

[2] G. Krüss, *Ueber die Schwefelverbindungen des Molybdäns*, Giessen, 1884; *Liebig's Ann.*, **225**. 1, 1884; *Ber.*, **16**. 2044, 1883; **17**. 1769, 1884; G. Krüss and H. Solereder, *ib.*, **19**. 2729, 1886; H. Debray, *Compt. Rend.*, **46**. 1102, 1858; L. Bodenstab, *Journ. prakt. Chem.*, (1), **78**. 186, 1859; H. ter Meulen, *Chem. Weekbl.*, **22**. 218, 1925; L. Fernandes, *Atti Accad. Lincei*, (6), **9**. 409, 1919; L. Fernandes and F. Palazzo, *Atti Accad. Lincei*, (6), **5**. 339, 1927; *Gazz. Chim. Ital.*, **57**. 567, 1927; F. Rodolico, *Atti Accad. Lincei*, (6), **7**. 660, 1928.

§ 25. Molybdenum Sulphates

According to J. J. Berzelius,[1] when dry hydrated molybdic oxide, $Mo(OH)_3$, is rubbed in a mortar with an eq. amount of sulphuric acid, a black mass of normal **molybdic sulphate** is formed. It is decomposed by water into a soluble acidic and an insoluble basic salt. A basic salt is also formed by rubbing an excess of molybdic oxide with sulphuric acid; and if the acid is in excess, an acidic salt is formed. These products represent more or less hydrolyzed and oxidized derivatives of the compound sought. W. Wardlaw and co-workers prepared molybdic oxydisulphate, $Mo_2O(SO_4)_2.5(\text{or } 6)H_2O$, from a soln. of 40 grms. of molybdenum trioxide in 81 c.c. of boiling sulphuric acid of sp. gr. 1·84, mixed with a little nitric acid made up to a litre with water, and electrolyzed in a diaphragm cell with smooth platinum electrodes. The electrolysis is conducted with the soln. in an atm. of carbon dioxide. The green soln. is concentrated between 55° and 70°. If the temp. is too high, the soln. becomes brown, and if the soln. be too much concentrated, red. The green, conc. soln. is poured into acetone. The freshly precipitated salt is intensely green, but when dried over phosphoric oxide, it becomes grey, with the loss of sulphate. When heated, it decomposes: $Mo_2O(SO_4)_2.nH_2O = Mo_2O_5 + 2SO_2 + nH_2O$. The substance is very hygroscopic and readily hydrolyzable. It is insoluble in alcohol, ether, or acetone, but dissolves readily in water; the soln. loses its green colour immediately on exposure to air, and a rusty-brown precipitate, readily soluble in acids, gradually forms. The oxydisulphate immediately precipitates the metals from soln. of copper sulphate and silver nitrate at the ordinary temp., and reduces mercuric and ferric salts to the "ous" state. On warming with sulphur or sodium sulphite, a soln. of the oxydisulphate, acidified with dil. sulphuric acid, evolves hydrogen sulphide. Barium chloride produces no precipitate in a freshly prepared soln. of the oxydisulphate, but barium sulphate is thrown down on warming. Lead acetate with acetic acid gives similar results. Sodium and potassium hydroxides give green deposits. Ammonia is without action in the cold, but produces a black precipitate on warming. Potassium ferricyanide gives a deep red coloration; a similar coloration is slowly produced by potassium ferrocyanide. F. Förster and E. Fricke, and A. Chilesotti did not succeed in preparing alums of tervalent molybdenum.

According to J. J. Berzelius, if molybdenum is dissolved in hot, conc. sulphuric acid; or in dil. sulphuric acid mixed with a little nitric acid; or if hydrated molybdenum dioxide is dissolved in dil. sulphuric acid, black **molybdenum disulphate** is formed. It forms a red soln. with water. J. Meyer and V. Stateczny prepared **sulphatomolybdic acid,** $H_2[MoO(SO_4)_2(MoO_4)]$, by cooling a soln. of molybdenum trioxide in hot, conc. sulphuric acid. It is not considered to be a pyrosulphatomolybdic acid, H_2MoSO_7. L. Forsén also prepared potassium sulphatomolybdate, $K_2H_2[SO_2(Mo_3O_{12})].3H_2O$.

G. Bailhache [2] found that when a rapid current of hydrogen sulphide is passed into a boiling soln. of molybdenum trioxide in six times its weight of sulphuric acid, **molybdenum trioxydisulphate,** $Mo_2O_3(SO_4)_2$, or $Mo_2O_5.2SO_3$, is obtained as a mass of black, olive prisms, slowly but completely soluble in water, and yielding a deep brown soln. if kept out of contact with air. When exposed to air, the compound deliquesces and its aq. soln. becomes green and then blue. The brown soln. is readily oxidized to molybdic acid; when mixed with an alkali molybdate, it yields the blue molybdenum oxide, and when mixed with an alkali it yields a soluble molybdate and a precipitate of hydrated molybdenum dioxide. When heated alone, the compound yields molybdic, sulphuric, and sulphurous oxides; hot sulphuric acid converts it into the compound $MoO_3.SO_3$; hydrogen at a red-heat converts it into molybdenum dioxide and sulphuric acid, and dry ammonia also reduces it at a dull red-heat. When heated with an intimate mixture of sodium chloride or bromide, it yields molybdenum oxychloride, MoO_2Cl_2, or the oxybromide, together with molybdenum dioxide, sodium sulphate, and sodium molybdate, the proportions of the two latter depending on the duration of the operation. A. Kurtenacker and F. Werner studied the catalytic decomposition of hydroxylamine by quinquevalent molybdenum sulphate.

According to E. Péchard,[3] when alcohol is gradually added to a soln. of molybdic acid in sulphuric acid and the liquid warmed on the water-bath for a short time, diluted, and neutralized with ammonia, a crystalline precipitate is produced which consists of a mixture of two **ammonium molybdosic sulphates,** one of the composition $5NH_3.MoO_2SO_3.7MoO_3.8H_2O$, crystallizing in blue, hexagonal plates, and the other, $3NH_3.MoO_2SO_3.7MoO_3.10H_2O$, in dark blue prisms; the latter is converted into the former by the further action of ammonia. Both these compounds are very soluble in water, but insoluble in soln. of ammonium salts; they are only very slowly decomposed by alkales or nitric acid at the ordinary temp., and are therefore more stable than the other blue compounds of molybdenum which have been described. Analogous compounds containing potassium, and both potassium and ammonium, have also been obtained, but the corresponding sodium salt is too soluble to admit of isolation. The prolonged reduction of molybdic acid by alcohol in the presence of sulphuric acid at the ordinary temp. results in the formation of **molybdosic sulphate,** $7MoO_3.2MoO_2.7SO_3.nH_2O$, crystallizing in slender, black needles; while if the operation is conducted at 100°, soln. are formed which are immediately decomposed by ammonia. M. K. Hoffmann repeated E. Péchard's observations. He also reported products with $(NH_4)_2O : MoO_2 : MoO_3 : SO_3 : H_2O$ in the proportions $1:1:7:1:n$; $1:5:1:7:1:15$; and $2:1:7:1:14$. He also obtained in a similar way **potassium molybdosic sulphate,** $K_2O.MoO_2.7MoO_3.SO_3.8H_2O$.

According to J. J. Berzelius,[4] if an excess of molybdenum trioxide be boiled with sulphuric acid, a turbid liquid is obtained which gelatinizes on cooling and deposits flakes of a basic sulphate which are sparingly soluble in water, but insoluble in alcohol. A soln. of molybdenum trioxide in an excess of dil. sulphuric acid is pale yellow, and dries to a lemon-yellow, crystalline mass, which deliquesces in air, and is only partially soluble in water. M. Ruegerberg and E. F. Smith said that precipitated molybdenum trioxide is easily soluble in sulphuric acid of sp. gr.

1·378. According to T. Anderson, if barium molybdate be decomposed by an excess of dil. sulphuric acid, and the soln. evaporated, crystals of **molybdenum trisulphate,** $Mo(SO_4)_3.2H_2O$, are formed. A. C. Schultz-Sellak, however, could not obtain this product. There is no satisfactory evidence that the normal salt has been obtained. M. K. Hoffmann, M. Ruegerberg and E. F. Smith, and A. Mazzucchelli and G. Zangrilli studied the properties of soln. of molybdenum trioxide in sulphuric acid. If hydrogen dioxide be added to the soln., the results are complicated by the decomposition of the complex **molybdenum persulphates,** and do not admit of any simple interpretation. A. Mazzucchelli and C. Barbero measured the potentials of the soln.—*vide supra,* permolybdates.

A. C. Schultz-Sellak evaporated a soln. of molybdenum trioxide in conc. sulphuric acid and obtained crystals of what he regarded as **molybdenum dioxysulphate,** or **molybdenyl sulphate,** $MoO_2(SO_4)$, but T. Anderson could not obtain crystals. W. Muthmann cooled a sat. soln. of molybdenum trioxide in boiling, conc. sulphuric acid, and washed with alcohol and ether the crystals of the salt which separated in six-sided prisms. When the salt is heated it decomposes with the expulsion of sulphur trioxide. The salt deliquesces in air, and becomes blue owing to the reducing action of dust. The aq. soln. becomes blue when warmed with molybdenum. R. Reichwald found that fumarine is coloured violet and then dark green by this salt. W. T. Schaller found that the mineral **ilsemannite,** previously assumed to be $MoO_2.4MoO_3$, or Mo_3O_{14}, found at Ouray, Utah, is rather a sulphate of the composition $MoO_2(SO_4).5H_2O$.

R. F. Weinland and H. Kühl added 5 to 8 mols of sulphuric acid to a mol of ammonium molybdate, and evaporated the mixture over sulphuric acid. He thus obtained **ammonium molybdatotrisulphate,** $(NH_4)_2O.2MoO_3.3SO_3.10H_2O$. By dissolving molybdenyl sulphate in conc. soln. of ammonium sulphate, the **ammonium molybdatosulphate,** $(NH_4)_2O.2MoO_3.SO_3.nH_2O$, is tetrahydrated or enneahydrated. If potassium sulphate be employed, the **potassium molybdatosulphate,** $K_2O.2MoO_3.SO_3.nH_2O$, is dihydrated or hexahydrated. A soln. of a mol of potassium molybdate in 5 to 8 mols of sulphuric acid furnishes **potassium molybdatotrisulphate,** $K_2O.2MoO_3.3SO_3.6H_2O$. The salts all form slender needles, which are decomposed by water with the precipitation of molybdic acid.

C. W. Blomstrand,[5] and A. Atterberg prepared **molybdous tetrabromosulphate,** $[Mo_3Br_4]SO_4.3H_2O$, by the action of sulphuric acid on an alkaline soln. of molybdous dihydroxytetrabromide.

REFERENCES.

[1] J. J. Berzelius, *Svenska Akad. Handl.*, 125, 300, 1825 ; *Pogg. Ann.*, **7**. 262, 1826 ; *Ann. Chim. Phys.*, (2), **29**. 369, 1825 ; W. Wardlaw, F. H. Nicholls and N. D. Sylvester, *Journ. Chem. Soc.*, **125**. 1910, 1924 ; F. Förster and E. Fricke, *Zeit. angew. Chem.*, **36**. 62, 458, 1923 ; A. Chilesotti, *Zeit. Elektrochem.*, **12**. 146, 173, 1906 ; L. Forsén, *Compt. Rend.*, **172**. 215, 327, 681, 1921 ; V. Stateczny, *Ueber einige Heteropolysäuren von Elementen der Schwefelgruppe*, Breslau, 1922 ; J. Meyer and C. Stateczny, *Zeit. anorg. Chem.*, **122**. 1, 1922.

[2] G. Bailhache, *Compt. Rend.*, **132**. 475, 1901 ; A. Kurtenacker and F. Werner, *Zeit. anorg. Chem.*, **160**. 333, 1927.

[3] E. Péchard, *Compt. Rend.*, **132**. 628, 1901 ; M. K. Hofmann, *Zur Analyse der niederen Molybdänoxydverbindungen und Beiträge zur Chemie der Salze derselben*, Bern, 26, 1903.

[4] J. J. Berzelius, *Svenska Akad. Handl.*, 125, 300, 1825 ; *Pogg. Ann.*, **7**. 262, 1826 ; *Ann. Chim. Phys.*, (2), **29**. 369, 1825 ; A. C. Schultz-Sellak, *Ber.*, **4**. 14, 1871 ; W. Muthmann, *Liebig's Ann.*, **238**. 108, 1887 ; R. Reichwald, *Russ. Pharm. Journ.*, **28**. 161, 177, 193, 209, 225, 1889 ; *Zeit. anal. Chem.*, **28**. 622, 1889 ; T. Anderson, *Berzelius' Jahresb.*, **22**. 161, 1843 ; R. F. Weinland and H. Kühl, *Zeit. anorg. Chem.*, **54**. 259, 1907 ; M. K. Hoffmann, *Zur Analyse der niederen Molybdänoxydverbindungen und Beiträge zur Chemie der Salze derselben*, Bern, 26, 1903 ; M. Ruegerberg and E. F. Smith, *Journ. Amer. Chem. Soc.*, **22**. 772, 1900 ; A. Mazzucchelli and G. Zangrilli, *Gazz. Chim. Ital.*, **40**. ii, 71, 1910 ; A. Mazzucchelli and C. Barbero, *Atti Accad. Lincei*, (5), **15**. ii, 39, 1906 ; J. Meyer and V. Stateczny, *Zeit. anorg. Chem.*, **122**. 1, 1922 ; W. T. Schaller, *Journ. Washington Acad.*, **7**. 417, 1917 ; *Chem. News*, **116**. 94, 1917.

[5] C. W. Blomstrand, *Journ. prakt. Chem.*, (1), **71**. 449, 1857 ; (1), **77**. 96, 1859 ; (1), **82**. 423, 1861 ; A. Atterberg, *Akad. Afhandl. Upsala*, 1, 1872 ; *Några Bidrag till kännedomen om Molybdän*, Upsala, 1872 ; *Bull. Soc. Chim.*, (2), **18**. 21, 1872.

§ 26. Molybdenum Carbonates and Nitrates

No **molybdenum carbonate** has been reported. J. J. Berzelius[1] dissolved hydrated molybdic oxide in dil. nitric acid and obtained a soln. of **molybdenum nitrate** which soon became purple-red. The soln. when concentrated becomes blue, then colourless, gives off nitric oxide, and deposits molybdenum trioxide. If molybdenum or the hydrated dioxide be digested in nitric acid, a reddish-brown soln. is obtained which gives off nitrous fumes when evaporated. C. F. Bucholz obtained a yellow residue—presumably molybdenum trioxide contaminated with iron—on evaporating the soln. K. Lindner and co-workers treated an alcoholic soln. of molybdous chloride with an alcoholic soln. of silver nitrate, and obtained on evaporation **molybdenum alcoholotetrachlorodinitrate,** $Mo_3Cl_4(NO_3)_2.C_2H_5OH$; and by adding ether to the alcoholic soln., **molybdenum tetrachlorodinitrate,** $Mo_3Cl_4(NO_3)_2$, was obtained as an amorphous, yellow powder. S. M. Tanatar and E. K. Kurowsky prepared **beryllium oxynitratomolybdate,** $Be(NO_3)_2.mBe_3(MoO_4)_2.nBeO$.

References.

[1] J. J. Berzelius, *Schweigger's Journ.*, **22.** 51, 1817; *Ann. Chim. Phys.*, (2), **17.** 5, 1921; *Pogg. Ann.*, **4.** 153, 1825; **6.** 331, 369, 1826; **7.** 261, 1826; C. F. Bucholz, *Scherer's Journ.*, **9.** 485, 1802; *Gehlen's Journ.*, **4.** 603, 1807; *Phil. Mag.*, **16.** 193, 1803; *Nicholson's Journ.*, **20.** 121, 188, 1808; *Journ. Mines*, **18.** 241, 1808; K. Lindner, E. Haller, and H. Helwig, *Zeit. anorg. Chem.*, **130.** 209, 1923; S. M. Tanatar and E. K. Kurowsky, *Journ. Russ. Phys. Chem. Soc.*, **41.** 813, 1909.

§ 27. Molybdenum Phosphates, and Phosphato- or Phospho-Molybdic Acids

As previously indicated, W. Wardlaw and R. L. Wormell[1] found that when molybdenyl monochloride is treated with an alkali phosphate, **molybdenyl phosphate,** $(MoO)_3PO_4.12H_2O$, is formed. A. Colani observed that when molybdenum trioxide is heated with metaphosphoric acid to a dull red-heat, it undergoes a very slight reduction, the loss in oxygen corresponding with the formation of the hypothetical oxide Mo_6O_{17}. When molybdenum dioxide is similarly heated, it yields the lower oxide Mo_2O_3, which gives **molybdic metaphosphate,** $Mo_2O_3.3P_2O_5$, and a higher oxide, which under the experimental conditions remains dissolved in the metaphosphoric acid. G. Saring prepared a complex potassium calcium phosphatomolybdate, $Ca_3(PO_4)_2.2CaO.2K_2O.MoO_3$, by fusing together the component residues. G. Denigès reported **phosphatomolybdosic acid,** $[(MoO_3)_4MoO_2]_2H_3PO_4.4H_2O$, to be obtained by treating sodium molybdate with crystalline sodium hydrophosphate in aq. soln. containing sulphuric acid and finely divided aluminium. The soln. was extracted with ether; the ether soln. extracted with water; and the aq. soln. evaporated under reduced press. The product forms sapphire-blue, rhombohedral crystals. The compound was examined by A. Verda. F. de Carli found that only an insignificant reduction of molybdenum trioxide occurs when it is fused with sodium metaphosphate, and even this is prevented with fusing the mixture in oxygen. Small proportions lower the m.p. of molybdenum trioxide (790°) down to the eutectic at 540° with 25 per cent. of the metaphosphate; the m.p. then rises to a maximum at 600° corresponding with **sodium molybdatometaphosphate,** $NaPO_3.MoO_3$, it then decreases to a second minimum at 320°, and then rises to 600°, the m.p. of the metaphosphate. The compound dissolves easily and completely in hot water; and its constitution is thought to be $Na.O.MoO_2.O.PO_2$. A. S. Schachoff discussed the preparation of sodium phosphomolybdate.

The complex **phosphatomolybdic acids** were discovered by J. J. Berzelius.[1] He found that when freshly precipitated and moist hydrated molybdenum trioxide is digested with a small proportion of phosphoric acid, a lemon-yellow, insoluble, complex acid is formed. This product dissolves in an excess of hot phosphoric acid forming a colourless liquid which on evaporation yields a tenacious, amorphous, transparent mass which is soluble in water and alcohol. The alcoholic soln. is yellow, but it turns blue on evaporation and leaves a brown residue which forms a blue soln. with water. The product was also examined by L. F. Svanberg and H. Struve, and E. Drechsel. F. Elias found that a soln. containing $P_2O_5 : MoO_3$=1 : 21·74 gives with a 10 per cent. soln. of ammonium nitrate a precipitate with the mol. proportions 1 : 22·28 ; using a cold, sat. soln. of potassium chloride as precipitate, the product has 1 : 22·71. The mother-liquors when evaporated give products with the respective ratios 1 : 18·44, and 1 : 20·3. It is therefore inferred that the soln. of molybdenum trioxide in phosphoric acid contains two or more phosphomolybdic acids. A. Miolati and R. Pizzigheli measured the sp. electrical conductivity of mixed soln. of phosphoric and molybdic acids when 1 c.c. of phosphoric acid soln. has 0·01961 grm. H_3PO_4, and 1 c.c. of molybdic acid soln. has 0·0288 grm. MoO_3 ; and when 1 c.c. of the molybdic acid soln. has 0·666 mol MoO_3 per mol of H_3PO_4. The curve shown in Fig. 31 has one break corresponding with $P_2O_5 : MoO_3$=1 : 20. A. Miolati and R. Pizzigheli also measured the sp. electrical conductivities of mixed soln. of molybdic acid and sodium hydrophosphate when 1 c.c. of the phosphate soln. has 0·02082 grm. Na_2HPO_4, and 1 c.c. of the molybdic acid has 0·01805 grm. MoO_3, or 0·5 c.c. has a mol of MoO_3 per mol of Na_2HPO_4. The curve shown in Fig. 32 has a break corresponding with $P_2O_5.MoO_3$=1 : 5 and 1 : 16 respectively. According to L. Malaprade, when phosphomolybdic acid, $P_2O_5.24MoO_3.3H_2O$, is neutralized with alkali, the electrometric curve shows no point of inflexion corresponding with the formation of the normal salt, but there is a point of inflexion corresponding with the formation of a salt of $P_2O_5.22MoO_3.7H_2O$; and a second one corresponding with the decomposition of the phosphomolybdic acid into phosphate and molybdate.

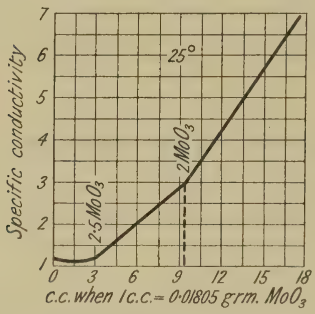


FIG. 31.—Electrical Conductivities of Mixed Solutions of Molybdic and Phosphoric Acids.

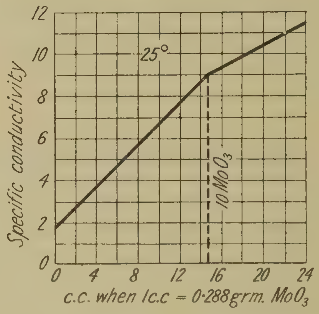


FIG. 32.—Electrical Conductivities of Mixed Solutions of Molybdic Acid and Sodium Hydrophospate.

According to A. Verda, when the ordinary phosphatomolybdic reagent (5 parts of phosphatomolybdic acid, 7 parts of nitric acid, 100 parts of water) is shaken with excess of ether, it is decolorized, the colour becoming conc. in a small quantity of dense liquid which separates at the bottom of the vessel. This proved to be a soln. of phosphatomolybdic acid in ether, for on evaporation of the ether there remained pure phosphatomolybdic acid as an amorphous yellow powder, more readily reducible than the ordinary phosphatomolybdic acid. Pure water dissolves out the phosphatomolybdic acid from the yellow liquid, but water sat. with ether is without action on it. Ether forms with solid phosphatomolybdic acid this yellow liquid, which, however, does not mix with the excess of ether. Soln. of phosphatomolybdates, acidified and treated with ether, can in this way be made to yield pure phosphatomolybdic acid. E. Péchard prepared the phosphatomolybdic acids as compounds of phosphoric acid with metamolybdic acid. A large number of salts has been reported, but, as in the case of the molybdate, there are doubts about the chemical individuality of many of them. The phosphatomolybdic acids with a high proportion of molybdate—say P : Mo=1 : 9 to 1 : 12—are yellow, whereas those with a lower proportion are white or colourless. According to A. Rosenheim, the yellow compounds can be regarded as derivatives of the septivalent PO_6-anion—or the H_7PO_6 acid—with the bivalent Mo_2O_7-radicle in place of oxygen; while the colourless series are derivatives of the tervalent PO_4-anion—or the H_3PO_4 acid—with the bivalent MoO_4-radicle.

Phosphatododecamolybdic acid	$H_7[P(Mo_2O_7)_6]$	$P_2O_5.24MoO_3.nH_2O$.
Phosphatohenamolybdic acid	$H_{12}[P_2(Mo_2O_7)_{11}]$	$P_2O_5.22MoO_3.nH_2O$.
Phosphatodecamolybdic acid,	$H_6[P(OH)(Mo_2O_7)_5]$	$P_2O_5.20MoO_3.nH_2O$.
Phosphatoenneamolybdic acid	$H_{12}[P_2O_2(Mo_2O_7)_9]$	$P_2O_5.18MoO_3.nH_2O$.
Phosphatohemiheptadecamolybdic acid	$H_{22}[P_4O_4(Mo_2O_7)_{17}]$	$2P_2O_5.34MoO_3.nH_2O$.
Phosphatohemipentamolybdic acid	$H_8[P_2O_4(MoO_4)_5]$	$P_2O_5.5MoO_3.nH_2O$.
Phosphatodimolybdic acid	$H_3[PO_2(MoO_4)_2]$	$P_2O_5.4MoO_3.nH_2O$.
Phosphatomolybdic acid	$H_3[PO_3(MoO_4)]$	$P_2O_5.2MoO_3.nH_2O$.

R. Finkener, and F. Kehrmann and E. Böhm obtained **phosphatododecamolybdic acid,** $P_2O_5.24MoO_3.nH_2O$, by adding yellow molybdenum trioxide to a boiling aq. soln. of phosphoric acid; evaporating, and cooling the soln. A. Miolati, and H. Debray, and M. G. Levi and E. Spelta obtained it by treating the ammonium salt with aqua regia, and repeatedly crystallizing the product from water acidulated with nitric acid. F. Hundershagen studied the conditions for its formation and separation as the ammonium salt in analytical work. According to E. Drechsel, and A. Rosenheim and J. Pinsker, phosphatododecamolybdic acid is also obtained by extracting with ether a soln. of molybdenum trioxide in phosphoric acid, or a soln. of a salt of the acid mixed with hydrochloric or nitric acid; and evaporating the ethereal layer. F. Kehrmann and E. Böhm used the following process:

Dissolve 50 grms. of sodium phosphate in water, and pour into the cold liquid, a cold, sat., aq. soln. of 200 grms. of ammonium paramolybdate in a thin stream with constant stirring. Wash the precipitate by repeated decantation with hot water acidulated with nitric acid. Dissolve it in hot aqua regia, and remove the volatile acids by repeated evaporation with water on a water-bath. Dissolve the dry residue in a little water, evaporate the filtered soln. on a water-bath. Filter by suction, wash the product with ice-cold water, and recrystallize twice from water acidulated with nitric acid.

R. Finkener, and F. Elias said that the soln. of phosphatododecamolybdic acid in a large proportion of nitric acid furnishes doubly refracting crystals of $P_2O_5.24MoO_3.32H_2O$, or the *dodecahydrate*, $H_7[P(Mo_2O_7)_6].12H_2O$. O. W. Gibbs, and G. Pohl said that if the conc. aq. soln. is allowed to stand it furnishes yellow octahedra of $P_2O_5.24MoO_3.62H_2O$—R. Finkener, and F. Elias gave $P_2O_5.24MoO_3.63H_2O$—or the *octocosihydrate*, $H_7[P(Mo_2O_7)_6].28H_2O$. A. Rosenheim and J. Pinsker also represented what they regarded as $P_2O_5.24MoO_3.63H_2O$; and G. Pohl, $P_2O_5.24MoO_3.64H_2O$. R. Finkener, and F. Elias represented the acid by the formula $H_3PO_4.12MoO_3.29H_2O$; and F. Kehrmann, by $PO(O.MoO_2.O.MoO_2.O.MoO_2.OH)_3$; A. Rosenheim gave $H_7[P(Mo_2O_7)_6]$. A. Miolati and R. Pizzighelli assume that the basicity of the acid is the difference between the negative valency of the acid groups and the positive valency of the central atom. This makes phosphatododecamolybdic acid septivalent. The septivalency of this acid is supported by the silver salt, $7Ag_2O.P_2O_5.24MoO_3$. According to the electrical conductivity rule—**1.** 15, 13—the guanidium salt behaves like a heptabasic acid. A. Miolati, and A. Rosenheim and J. Jaenicke found that the neutralization curve for the aq. soln. of the acid and a soln. of sodium hydroxide indicated that the acid is at least sexivalent and octocosihydrated. Phosphatododecamolybdic acid forms dark yellow, cubic octahedra. R. Finkener found that the salt loses all but 3 mols. of water at 140°, and A. Miolati added that no other chemical change occurs. The crystals begin to melt at 78°, and at 98° form a clear liquid from which, at 90°, crystals of the *dodecahydrate,* $H_7P(Mo_2O_7)_6.12H_2O$, are formed. The octocosihydrate is readily soluble in water and the same hydrate is deposited when the aq. soln. is crystallized. The soln. in conc. nitric acid deposits rhombic plates of the *docosihydrate,* $H_7P(Mo_2O_7)_6.22H_2O$. A. Rosenheim and J. Jaenicke gave for the eq. conductivity, λ mhos, of one-seventh a mol of the acid in v litres of water at 25°,

v . .	32	64	128	256	512	1024
λ . .	190·6	211·3	229·1	248·5	249·5	258·1

A. Rosenheim and A. Bertheim found that the dodeca-acid is gradually hydrolyzed in aq. soln. to form the ennea-acid—*vide infra*—and this explains the break in the conductivity curve, observed by A. Miolati and R. Pizzighelli—*vide supra,* when molybdic acid is successively added to phosphoric acid. T. G. y Arnal studied the reactions of nitrophosphomolybdic acid with various salts. A. Rosenheim and E. Brauer found the $H^{\cdot}$-ion conc. of the acid to be $5{\cdot}8\times10^{-3}$ for a $0{\cdot}005N$-soln. at 25°. The acid does not dissolve in *water.* The following reactions of a soln. of the acid with metallic salts, etc. were recorded by F. Kehrmann and E. Böhm : With *sodium chloride* no precipitation occurs since the sodium salt is very soluble ; *potassium and ammonium chlorides* give a yellow, very sparingly soluble, pulverulent precipitate ; *barium chloride* gives no precipitation since the barium salt is very soluble ; but it can be salted out by barium chloride ; *silver nitrate* gives a yellow, pulverulent, sparingly soluble precipitate ; *lead nitrate, mercuric chloride,* and the *sulphates of copper, zinc, cadmium, cobalt,* and *nickel* give no precipitate because the resulting salts are very soluble ; *methylamine, dimethylamine, pyridine,* and *quinoline* give yellow, pulverulent or flocculent precipitates almost insoluble ; *aniline* and *p-toluidine* give no precipitate in dil. soln., but with conc. soln. a yellow oil separates which soon crystallizes and becomes blue by reduction ; and β-napthylamine gives an oily precipitate which rapidly forms yellow, sparingly soluble crystals. F. Parmentier found that the sat. ethereal soln. has a sp. gr. of 1·3, and he measured the solubility in *ether* of what he regarded as phosphatodecamolybdic acid, but which was probably phosphatododecamolybdic acid ; and found that 100 grms. of ether dissolved S grms. of the acid :

	0°	8·1°	19·3°	27·4°	32·9°
S	80·6	84·7	96·7	103·9	107·9

According to R. Finkener, **ammonium phosphatododecamolybdate,** $m(NH_4)_2O.P_2O_5.24MoO_3.nH_2O$, is obtaine dfrom acid soln. when ammonia is added to a soln. of phosphatododecamolybdic acid. The composition of the precipitate was discussed by A. König, F. Elias, T. Salzer, H. Debray, C. Friedheim, H. von Jüptner, F. Feigl, A. von Lipowitz, V. Eggertz, E. Spiess, F. Hundeshagen, and C. F. Rammelsberg ; A. Villiers and F. Borg gave $3(NH_4)_2O.P_2O_5.24MoO_3.3H_2O$; H. C. Babbitt gave $3(NH_4)_2O.P_2O_5.24MoO_3.nH_2O$; and O. W. Gibbs, $2\frac{1}{2}(NH_4)_2O.P_2O_5.24MoO_3.8\frac{1}{2}H_2O$. According to S. Posternak, ammonium phosphatomolybdate precipitated from phosphate soln. in the absence of ammonium salts always contains phosphorus and molybdic oxide in a constant ratio. It consists of a variable mixture of di- and tri-ammonium phosphatomolybdates, varying according to the composition of the ammonium molybdate soln. used. In the presence of 5 per cent. or more of ammonium nitrate or sulphate the phosphatomolybdate precipitate obtained is a complex mixture of the types $16(NH_4)_3(MoO_3)_{12}PO_4.NH_4(MoO_3)_4NO_3$ and $8(NH_4)_3(MoO_4)_{12}PO_4.(NH_4)_2(MoO_3)_8SO_4$, respectively. In all cases the molybdic acid behaves as though, in acid medium, it existed in the tetramolybdic state, and in this form combined with the hydroxyl groups of all the mineral acids present.

A. von Endredy represented the formula $(NH_4)_3H_4[P(Mo_2O_7)_6].4H_2O$, and found that the precipitate is very prone to adsorb molybdenum trioxide. C. Friedheim, A. S. Schachoff, and G. Wirtz prepared rhombohedral crystals of **sodium phosphatododecamolybdate,** $5Na_2O(P_2O_5.24MoO_3)_2.100$ or $101H_2O$, by evaporating over sulphuric acid a soln. of a mol of sodium hydrophosphate and 10 mols of molybdic acid. M. Seligsohn obtained an *ammonium sodium phosphatomolybdate* approximating $6(NH_4)_2O.15Na_2O.P_2O_5.60MoO_3.18H_2O$. A. Miolati, and A. Rosenheim and J. Pinsker represented the sodium salt by the formula $Na_3H_4[P(Mo_2O_7)_6].19H_2O$, and the electrical conductivities of the soln. for one-third a mol of the salt in v litres of water at 25° were :

	v	32	64	128	256	512	1024
λ	A.M.	244·2	270·4	298	321·8	344·2	370·8
	A.R. and J.P.	250	275·2	301·4	325·2	350·6	380·0

O. W. Gibbs obtained yellow **potassium phosphatododecamolybdate,** $2K_2O.P_2O_5.24MoO_3.4H_2O$, by boiling for a long time a mixture of potassium molybdate and hydrosphosphate with an excess of nitric acid. F. Kehrmann and E. Böhm observed that what is presumably **copper phosphatododecamolybdate** is precipitated by copper sulphate from a soln. of the acid. The precipitate is soluble in water. A. Miolati and R. Pizzighelli obtained **silver phosphatododecamolybdate,** $7Ag_2O.P_2O_5.24MoO_3$, from a soln. of silver nitrate and phosphatododecamolybdic acid, or the ammonium salt. F. Kehrmann and E. Böhm reported **barium phosphatododecamolybdate,** $3BaO.P_2O_5.24MoO_3.nH_2O$, to be formed by treating the phosphatododecamolybdic acid with an excess of barium chloride. The pale yellow octahedra lose water of crystallization when exposed to air ; and they lose all their water at dull redness, without melting. The salt is soluble in water. M. Seligsohn obtained **ammonium barium phosphatomolybdate,** $3(NH_4)_2O.30BaO.P_2O_5.30MoO_3.nH_2O$, from a soln. of ammonium phosphatododecamolybdate and barium chloride. F. Parmentier, and A. Miolati and R. Pizzighelli obtained what was probably **mercurous phosphatododecamolybdate** by adding phosphatododecamolybdic acid to a soln. of a mercurous salt; and C. Kehrmann and E. Böhm, by using a mercuric salt soln. obtained **mercuric phosphatododecamolybdate,** $3HgO.P_2O_5.24MoO_3$, as a precipitate soluble in water. H. Beuf found that a boiling, neutral soln of a lead salt furnishes a precipitate of what is nearly **lead phosphatododecamolybdate,** namely, $25PbO.P_2O_5.24MoO_3.7H_2O$, when treated with an aq. soln. of phosphatomolybdic acid. The washed precipitate dried at 90° to 100° forms a dense white powder which is insoluble in water (1 in 500,000) and aq. ammonia, but dissolves in nitric and in acetic acids; and at a high temp., it loses 7 mols of H_2O. The **vanadium phosphatomolybdates** are discussed in connection with vanadium.

A. Arnfeld reported **manganese phosphatododecamolybdate,** $3MnO.P_2O_5.24MoO_3.58$ or $60H_2O$, to be formed by boiling a soln. of 40 grms. of manganese hydrophosphate with molybdenum trioxide, and allowing the filtered soln. to evaporate over sulphuric acid. The yellow octahedra effloresce in air. They dissolve in water ; and at 90° lose 16·8 per cent. of water, and at 140°, all the water is expelled. By boiling freshly-precipitated ferric phosphate, molybdenum trioxide, and water, and evaporating the filtered soln., a yellow powder was deposited ; the filtered liquid, when concentrated, deposits octahedral crystals of **ferric phosphatododecamolybdate,** $Fe_2O_3.P_2O_5.24MoO_3.58H_2O$. Water decomposes the salt. Instead of evaporating the soln., ether can be added, and the precipitated oil allowed to crystallize. A. Arnfeld prepared **cobalt phosphatododecamolybdate,** $3CoO.P_2O_5.24MoO_3.58$ to $60H_2O$, by the saturating with molybdenum trioxide 40 grms. of cobalt phosphate in boiling water ; and concentrating the brown soln. over sulphuric acid. The yellowish-brown, pyramidal crystals effloresce in air. The yellow aq. soln. becomes red when treated with acids. A. Arnfeld prepared green crystals of **nickel phosphatododecamolybdate,** $3NiO.P_2O_5.24MoO_3.58$ to

$60H_2O$, in an analogous way. The salt effloresces in air; loses all its water at 150°; and is soluble in water.

G. Pohl reported that if commercial phosphatomolybdic acid be recrystallized, the compound $P_2O_5.23MoO_3.nH_2O$ can be obtained from the mother-liquors; and similarly also **phosphatohenamolybdic acid,** $P_2O_5.22MoO_3.58H_2O$. C. F. Rammelsberg obtained **ammonium phosphatohenamolybdate,** $3(NH_4)_2O.P_2O_5.22MoO_3.12H_2O$, by precipitation from a nitric acid soln. of ammonium molybdate on the addition of phosphoric acid. According to A. E. Nordenskjöld, the axial ratios of the monoclinic prisms are $a : b : c = 0{\cdot}5092 : 1 : 0{\cdot}8466$, and $\beta = 90° \ 59'$. The yellow, air-dried salt loses all its water over sulphuric acid, and it is then stable at 100°, but gives off ammonia at 120°. O. W. Gibbs reported yellow crystals of **potassium phosphatohenamolybdate,** $5K_2O(P_2O_5.22MoO_3)_2.22H_2O$, to be formed by boiling for a short time a mixture of potassium molybdate and hydrophosphate with an excess of nitric acid; and C. F. Rammelsberg, $3K_2O.P_2O_5.22MoO_3.12H_2O$, by adding phosphoric acid to a nitric acid soln. of potassium molybdate. The crystals resemble those of the ammonium salt. They lose their water completely at 120°–140°, and suffer no further loss in weight at a red-heat. F. Ephraim and H. Herschfinkel obtained **rubidium phosphatohenamolybdate,** $7Rb_2O.22MoO_3.P_2O_5.12H_2O$, by gradually adding 2·5 grms. of molybdic acid to a soln. of 30 c.c. of rubidium carbonate (containing 5·5 grms. Rb_2O per litre) and 12 c.c. of 3·3 per cent. phosphoric acid. O. W. Gibbs obtained small tabular crystals of **silver phosphatohenamolybdate,** $7Ag_2O.P_2O_5.22MoO_3.14H_2O$, from a soln. of silver nitrate and the corresponding phosphatomolybdic acid. The salt is soluble in hot water.

H. Debray obtained *doublement obliques* (triclinic) prisms of what was regarded as **phosphatodecamolybdic acid,** $P_2O_5.20MoO_3.24$, 41, 51, or $52H_2O$, or $H_6[P(OH)(Mo_2O_7)_5].nH_2O$, by the action of aqua regia on ammonium phosphate. G. Pohl, and F. Parmentier also prepared this product. These phosphatomolybdic acids, as well as the salts which have been reported, are probably impure phosphatododecamolybdic acid or phosphatododecamolybdates, or else the formulæ are based on unsatisfactory analyses. A. Rosenheim and A. Bertheim, and A. Miolati considered phosphatodecamolybdic acid to be a mixture of phosphatododecamolybdic and phosphatoenneamolybdic acids. O. W. Gibbs described **ammonium phosphatodecamolybdate,** $8(NH_4)_2O.(P_2O_5.20MoO_3)_3.12H_2O$, as a yellow salt; and the salt $(NH_4)_3H_3[P(OH)(Mo_2O_7)_5]$ was described by L. F. Svanberg and H. Struve, F. L. Sonnenschein, M. Seligsohn, M. Nutzinger, and A. von Lipowitz. H. Rose prepared it from a soln. of molybdic acid, ammonia, orthophosphoric acid not in excess in an acid soln.—preferably nitric acid. Pyrophosphates and metaphosphates do not give the yellow, pulverulent precipitate, unless, added H. Struve, they are first transformed into orthophosphates. According to H. Debray, if the transformation is slow, the precipitate may be crystalline. A. von Lipowitz found that the precipitate can be obtained free from an excess of molybdic acid by dissolving 2 parts of molybdic acid, and one part of tartaric acid in 15 parts of warm water, adding 10 parts of aq. ammonia of sp. gr. 0·97, and then 15 parts of nitric acid; heating the soln. to its b.p. when some molybdic acid is precipitated; again heating the filtered soln. to its b.p.; and adding one part of phosphoric acid to 100 parts of the filtrate. The precipitate is washed with 2 per cent. nitric acid, and dried over sulphuric acid. H. Debray obtained the salt by adding phosphatodecamolybdic acid to a strongly acid soln. of an ammonium salt. The canary-yellow precipitate, said L. F. Svanberg and H. Struve, is an amorphous powder. When heated to redness, ammonia and water are given off, and the brown or green residue forms with nitric acid a soln. which is yellow when hot, and colourless when cold; and which, on evaporation, furnishes yellow rhombohedra of phosphatodecamolybdic acid. Ammonium phosphatodecamolybdate is sparingly soluble in water or acids; and it is easily soluble in aq. ammonia, and alkali-lye. If an excess of ammonium molybdate be present, E. Richter said that the precipitate is nearly insoluble in aq. ammonia, and it is also insoluble in a feebly acid soln. of ammonium nitrate. H. Struve said that acetic acid favours the precipitation; while C. R. Fresenius found that in the presence of ammonium molybdate and free nitric acid, the precipitation is retarded by hydrochloric acid, ammonium and metal chlorides, tartaric acid, ammonium tartrate or citrate, and an excess of phosphoric acid. According to F. L. Sonnenschein, the following favour the dissolution of the precipitate: a large excess of water, or alcohol; alkali hydroxides, carbonates, or ortho-, meta-, or pyrophosphates; barium borate; sodium dithionate, thiosulphate, acetate, arsenite, or arsenate; potassium sodium tartrate; ammonium oxalate; phosphoric acid, or conc. sulphuric acid; while ammonium molybdate or sulphate; potassium sulphate; tartrate, oxalate, nitrate, chlorate, chloride, bromide, or iodide; sodium bromide, or nitrate; or nitric, hydrochloric, boric, tartaric, oxalic, or dil. sulphuric acid, do not have a solvent action. F. L. Sonnenschein also described a **sodium phosphatodecamolybdate.** A. S. Schachoff recommended the following mode of preparation:

Ammonium molybdate was prepared direct from 600 grms. of commercial molybdic acid, and an aq. soln. was treated with 100 grms. of sodium phosphate, and subsequently with 400 c.c. of hydrochloric acid. The precipitated ammonium phosphatomolybdate, washed free from chloride, was dissolved in a soln. of 200 grms. of sodium hydroxide in a small quantity of water, the liquid evaporated to dryness, and the residue heated to expel the residual ammonia. The salt was then crystallized from water, the final yield being 115–120 per cent. of the molybdic acid taken. The proportions of water of crystallization and of sodium present vary in different preparations.

L. F. Svanberg and H. Struve reported **potassium phosphatodecamolybdate,** $3K_2O.P_2O_5.20MoO_3.3H_2O$, to be formed by boiling the ammonium salt with potassium hydroxide so long as ammonia is given off, mixing the colourless soln. with nitric acid, and washing the precipitate with water acidulated with nitric acid. H. Debray obtained it by adding phosphatodecamolybdic acid to a soln. of a potassium salt—a precipitate is formed if only 0·002 part of potassium be present. The yellow, four-sided prisms lose water when heated, and melt at dull redness. L. F. Svanberg and H. Struve said that the salt is insoluble in water, and H. Debray added that it is easily soluble in alkali-lye. F. Ephraim and H. Herschfinkel prepared **rubidium phosphatodecamolybdate,** $3Rb_2O.P_2O_5.20MoO_3.12H_2O$, as a yellow crystalline powder, from a soln. of 200 c.c. of rubidium carbonate (with 10·94 grms. Rb_2O) and 8·46 grms. of molybdenum trioxide, and 0845 grm. of P_2O_5 in 25 c.c. of water, and dropping in 50 c.c. of nitric acid of sp. gr. 1·20. H. Debray said that microscopic crystals of **silver phosphatodecamolybdate,** $7Ag_2O.P_2O_5.20MoO_3.24H_2O$, are precipitated by the phosphatodecamolybdic acid from a soln. of silver nitrate; and if a nitric acid soln. of this salt be evaporated, yellow crystals of $2Ag_2O.P_2O_5.20MoO_3.7H_2O$ are formed. Similarly, he obtained **thallous phosphatodecamolybdate,** by adding an acid soln. of a thallous salt to the phosphatodecamolybdic acid.

F. Kehrmann prepared **phosphatoenneamolybdic acid,** $P_2O_5.18MoO_3.nH_2O$, or $H_{12}[P_2O_2(Mo_2O_7)_9].nH_2O$, by treating a warm soln. of the potassium salt, in a small proportion of water and sulphuric acid, with five times its vol. of alcohol. An equal vol. of ether was then added to the soln., and after allowing the liquid to stand in a freezing mixture for some time, evaporating it over sulphuric acid. It was also obtained by treating yellow hydrated molybdenum trioxide with boiling phosphoric acid, when the dodeca-acid first precipitates; after the product has stood some weeks it becomes liquid, and when this is allowed to crystallize, the ennea-acid separates out. The acid was also prepared by G. Pohl, and F. Elias. The ennea-acid appears to be a hydrolysis product of the dodeca-acid, for A. Rosenheim, and A. Miolati found that if an aq. soln. of the dodeca-acid is allowed to stand for some weeks, it gradually loses its power to give a precipitate with ammonium chloride and it has then passed into the ennea-acid. The change is accelerated by adding a small proportion of phosphoric acid to the soln. E. Drechsel obtained it by extracting the soln. in dil. hydrochloric acid by means of ether, and the aq. ethereal soln. evaporated. Phosphatoenneamolybdic acid furnishes orange-red, hygroscopic prisms, and, in allusion to the colour—*luteus*, yellow—it is also called *luteophosphomolybdic acid.* The acid is freely soluble in water in any proportions. It effloresces over sulphuric acid, and it then rapidly dissolves in water without undergoing any chemical change. The acid is quantitatively precipitated as the potassium salt by the addition of potassium chloride. The orange-yellow crystals are probably those of the *tetracosi-hydrate*, although the analyses show between 24 and $30H_2O$. If the orange-yellow prisms be kept under the mother-liquid at 0° for some time, yellow crystals of the *tetratriconti-hydrate* are formed. According to A. Rosenheim and A. Traube, the progressive neutralization of the ennea-acid by alkali shows that its basicity is more than six. The electrical conductivity of the sodium salt, and the composition of the phosphato-enneamolybdates agree with the assumption that the anion is either decabasic, $[P(OH)(Mo_2O_7)_4–Mo_2O_7–P(OH)(Mo_2O_7)_4]$, or else dodecabasic: $[PO(Mo_2O_7)_4–Mo_2O_7–PO(Mo_2O_7)_4]$ or $[P(OH)_2(Mo_2O_7)_4–Mo_2O_7–P(OH)_2(Mo_2O_7)_4]$. A. Rosenheim and A. Traube found the eq. conductivity, λ mhos, of a soln. of one-twelfth of a mol of the acid in v litres at 25°, to be:

v	32	64	128	256	512	1024
λ	197·9	210·0	218·0	226·6	236·9	248·8

The following are some reactions of soln. of the ennea-acid with soln. of metallic salts, etc. recorded by F. Kehrmann and E. Böhm: There is no precipitation with *sodium chloride* owing to the solubility of the sodium salt; similarly also with *ammonium chloride*, but the ammonium salt can be salted out from the soln. by ammonium chloride; *potassium chloride* gives no precipitate, but the soluble potassium salt can be salted out by potassium chloride; *barium chloride* gives no precipitate since the barium salt is so soluble; similar remarks apply to *mercuric chloride*, the *sulphates of copper, zinc, and cadmium,* and to *lead nitrate*—the soln. with the latter salt soon decomposes with the separation of a white powder; *silver nitrate* gives a yellow, flocculent precipitate soluble in water, but insoluble in a dil. soln. of silver nitrate; mercurous nitrate gives a yellow, pulverulent precipitate very sparingly soluble in cold water but rather more soluble in hot water; *thallous sulphate* gives a dark yellow, crystalline precipitate, appreciably soluble in hot water; *stannous chloride* gives no precipitate but a blue reduction product is formed in soln.; similarly with *antimonous chloride; stannic chloride* gives no perceptible change; *methylamine,* and *dimethylamine* give no precipitates; *pyridine,* and *quinoline* give yellow flocculent precipitates almost insoluble in cold or boiling water; *aniline,* and *p-toluidine* give yellow oily drops with fairly conc. soln., and these soon form scaly crystals, and a blue reduction product; and *β-naphthylamine* gives a yellow, oily precipitate which, when warm, soon forms a crystalline powder.

F. Kehrmann and E. Böhm treated barium phosphatododecamolybdate with dil. sulphuric acid, and saturated the filtered soln. with solid ammonium chloride; orange, prismatic crystals of **ammonium phosphatoenneamolybdate,** $(NH_4)_6H_6[P_2O_2(Mo_2O_7)_9].11H_2O$, were formed. The aq. soln. can be kept days in the cold, but when heated, ammonium phosphatodecamolybdate is precipitated. E. Ephraim and M. Brand obtained orange pyramidal crystals of **lithium phosphatoenneamolybdate,** $Li_6H_6[P_2O_2(Mo_2O_7)_9].24H_2O$, which lose 18 mols. of water at 100°, and the remainder at a red-heat; the salt is soluble in cold water. F. Elias also obtained a similar salt from a soln. of lithium carbonate and molybdic acid mixed with phosphoric acid. C. Friedheim reported prismatic crystals of **sodium phosphatoenneamolybdate,** $3Na_2O.P_2O_5.18MoO_3.25$ or $26H_2O$, from a soln. of sodium phosphate and molybdic acid. F. Kehrmann and E. Böhm prepared **potassium phosphatoenneamolybdate,** $3K_2O.P_2O_5.18MoO_3.14H_2O$, by adding potassium chloride to the corresponding ammonium salt. The orange-red, prismatic crystals are more stable than the ammonium salt. The salt is sparingly soluble in cold water, but more soluble in hot water. L. Duparc and F. Pearce gave for the axial ratios of the triclinic crystals $a:b:c=0·5938:1:0·6479$, and $\alpha=60°\ 50'$, $\beta=114°\ 22'$, and $\gamma=115°\ 26'$. F. Elias represented the salt as containing $11H_2O$ and also $15H_2O$. F. Ephraim and H. Herschfinkel boiled a soln.

of rubidium phosphatodecamolybdate with rubidium carbonate, evaporated the filtered soln., and obtained **rubidium phosphatoenneamolybdate,** $6Rb_2O.P_2O_5.18MoO_3.10H_2O$. F. Kehrmann and E. Böhm observed that presumably **copper phosphatoenneamolybdate** is precipitated by copper sulphate from a soln. of the acid. The precipitate is soluble in water: by using mercurous nitrate, they obtained **mercurous phosphatoenneamolybdate;** and with mercuric chloride, **mercuric phosphatoenneamolybdate,** $3HgO.P_2O_5.18MoO_3$.

A. Arnfeld treated the mother-liquor obtained in the preparation of manganous phosphatododecamolybdate with potassium chloride, and allowed the filtered liquid to crystallize. Prismatic crystals of **manganese phosphatoenneamolybdate,** $3MnO.P_2O_5.18MoO_3.38H_2O$, were obtained. The crystals lose 19 mols. of water at 90°; 33 mols. at 100°; 35 mols. at 120°; and all the water is expelled at 150°. The salt forms a yellow soln. with water. Attempts to prepare **ferric phosphatoenneamolybdate** were not successful. A. Arnfeld obtained **cobalt phosphatoenneamolybdate,** $3CoO.P_2O_5.18MoO_3.38H_2O$, by allowing the mother-liquor from the preparation of the phosphatododecamolybdate to stand over sulphuric acid. He also obtained **nickel phosphatoenneamolybdate,** $3NiO.P_2O_5.18MoO_3.34H_2O$, in green, triclinic crystals in an analogous manner. The salt loses 30 mols. of water at 90°; and 34 mols. at 140°. The crystals effloresce in air, and form a green soln. with water.

F. Kehrmann and E. Böhm found that the hydrolysis of a soln. of a phosphatoenneamolybdate furnishes unstable salts of **phosphatohemiheptadecamolybdic acid,** $2P_2O_5.34MoO_3.nH_2O$, or $H_{22}[P_4O_4(Mo_2O_7)_{17}].nH_2O$. If a cold, sat. soln. of potassium hexahydrophosphatoenneamolybdate is mixed with a soln. of potassium hydrocarbonate, lemon-yellow scales of **potassium phosphatohemiheptadecamolybdate,** $5K_2O.P_2O_5.17MoO_3.26H_2O$, or $K_{20}H_2[P_4O_4(Mo_2O_7)_{17}].51H_2O$, are formed. The salt slowly decomposes at ordinary temp., and immediately on boiling. F. Elias also prepared $3K_2O.P_2O_5.17MoO_3.12H_2O$. F. Kehrmann and E. Böhm also prepared **ammonium phosphatohemiheptadecamolybdate,** $5(NH_4)_2O.P_2O_5.17MoO_3.nH_2O$, in bright yellow nodules by the action of ammonium hydrocarbonate on the ammonium phosphatoenneamolybdate; and similarly with **sodium phosphatohemiheptadecamolybdate,** $5Na_2O.P_2O_5.17MoO_3.nH_2O$. By treating sodium phosphatoenneamolybdate with ammonium chloride and ammonium hydrocarbonate, **ammonium sodium phosphatohemiheptadecamolybdate,** $(NH_4)_{16}Na_6[P_4O_4(Mo_2O_7)_{17}].33H_2O$, is formed; and similarly with **potassium sodium phosphatohemiheptamolybdate,** $K_{16}Na_6[P_4O_4(Mo_2O_7)_{17}].36H_2O$. By double decomposition with silver nitrate, **silver phosphatohemiheptadecamolybdate,** $Ag_{22}[P_4O_4(Mo_2O_7)_{17}].40H_2O$, is formed, and similarly with the *guanidinium salt*, $(CN_3H_6)_{22}[P_4O_4(Mo_2O_7)_{17}].40H_2O$.

O. W. Gibbs reported *ammonium phosphatoctomolybdate*, $3(NH_4)_2O.P_2O_5.16MoO_3$ $14H_2O$, as a white precipitate, by a process like that used for the phosphatohemipentamolybdate; and J. Meschoirer, $5(NH_4)_2O.P_2O_5.16MoO_3$, by the action of 25 grms. of ammonium dihydrophosphate on a cold, conc. soln. of 105 grms. of ammonium molybdate.

J. Meschoirer reported white crystals of *ammonium phosphatoheptamolybdate*, $9(NH_4)_2O.2P_2O_5.28MoO_3.8H_2O$, by the action of 25 grms. of ammonium dihydrophosphate on a hot, conc soln. of 105 grms. of ammonium molybdate. F. Ephraim and H. Herschfinkel reported *cæsium phosphatoheptadecamolybdate*, $2Cs_2O.P_2O_5.17MoO_3.3H_2O$, as a yellow, microcrystalline powder to be formed by the method employed for rubidium phosphatodecamolybdate.

F. Ephraim and M. Brand reported *lithium phosphatohexamolybdate*, $3Li_2O.P_2O_5.12MoO_3.18H_2O$, to be formed as a lemon-yellow microcrystalline powder by treating a conc. soln. of the phosphatohemipentamolybdate with dil. nitric acid. O. W. Gibbs found that soln. of what he regarded as *ammonium phosphatohexamolybdate*, $2(NH_4)_2O.2P_2O_5.12MoO_3.3H_2O$, is dissolved by a soln. of copper sulphate.

O. W. Gibbs found that what he regarded as *ammonium phosphatotetramolybdate*, $2(NH_4)_2O.P_2O_5.8MoO_3.5H_2O$, gave no precipitate with a soln. of copper sulphate, nor is it reduced by boiling with or without hydrochloric acid. Ammonia gives a green, flocculent precipitate.

F. Ephraim and H. Herschfinkel obtained *cæsium phosphatotrimolybdate*, $3Cs_2O.P_2O_5.$

$6MoO_3.8H_2O$, as a white micro-crystalline powder, by the method used for rubidium phosphatotetritaenneamolybdate excepting that cæsium hydroxide is mixed first with the phosphoric acid, and the soln. then sat. with molybdenum trioxide. H. Perlberger obtained *ammonium cadmium phosphatotrimolybdate*, $2(NH_4)_2O.CdO.P_2O_5.6MoO_3.8H_2O$, by the action of ammonium phosphatohemipentamolybdate on cadmium chloride.

N. Seligson prepared a complex of molybdic acid with inositol phosphate, $C_6H_6(NH_4HPO_4)_6.6MoO_3.15H_2O$.

H. Debray prepared salts of **phosphatohemipentamolybdic acid,** $P_2O_5.5MoO_3.nH_2O$, but added that the free acid cannot be obtained from the salts because it is decomposed into phosphoric acid and presumably phosphatododecamolybdic acid. If a yellow soln. of a phosphatomolybdate be treated with conc. aq. ammonia, hydrolysis occurs, the soln. becomes colourless, and a white phosphatohemipentamolybdate is formed. A. Miolati and R. Pizzighelli, and C. Friedheim showed that the anion is probably octobasic, and, in the language of the co-ordination theory, can be represented $[PO_2(MoO_4)_2–MoO_4–PO_2(MoO_4)_2]$, or $[P_2O_4(MoO_4)_5]$. According to C. Friedheim, when less than two mols of molybdenum trioxide react with one of potassium hydrophosphate there are formed **potassium dihydrophosphatohemipentamolybdate,** $K_6H_2[P_2O_4(MoO_4)_5].6H_2O$, and **potassium trihydrophosphatohemipentamolybdate,** $K_5H_3[P_2O_4(MoO_4)_5].4H_2O$. C. F. Rammelsberg obtained *white* prisms of the trihydrophosphatohemipentamolybdate by adding phosphoric acid to a soln. of potassium trimolybdate in as small a quantity as practicable of potassium hydroxide soln. The rhombic bipyramids had the axial ratios $a:b:c=0·9833:1:0·8209$. The salt loses water at 120°. F. A. Zenker obtained the dihydrophosphohemipentamolybdate by evaporating a soln. of phosphoric acid and molybdenum trioxide in hydrochloric acid, and saturating the syrupy liquid with potassium hydroxide; H. Debray, by melting the ammonium salt with potassium nitrate, and crystallizing from aq. soln.; and C. F. Rammelsberg, by melting a mol of potassium carbonate, 2 mols of molybdenum trioxide, and mixing a soln. of the product with phosphoric acid. The colourless, rhombic bipyramids have the axial ratios $a:b:c=0·7199:1:0·7151$. The aq. soln. has an acid reaction, and gives a precipitate with nitric or hydrochloric acid. C. Friedheim observed that if two mols of molybdenum trioxide are mixed with a mol of potassium hydrophosphate, the hemiheptadecamolybdate is formed, as well as **potassium tetrahydrophosphatohemipentamolybdate,** $K_4H_4[P_2O_4(MoO_4)_5].4H_2O$—some phosphatodimolybdate is formed. F. A. Zenker reported **ammonium dihydrophosphatohemipentamolybdate,** $(NH_4)_6H_2[P_2O_4(MoO_4)_5].6H_2O$, to be formed by the spontaneous evaporation of an ammonia soln. of ammonium phosphatodecamolybdate. The first crop of crystals is ammonium paramolybdate. The next crop of crystals can be purified by crystallization from hot water and a little ammonia. O. W. Gibbs, H. Debray, and A. Werncke prepared it from a soln. of ammonium molybdate and ammonium phosphate. H. Perlberger, and J. Meschoirer also prepared the hexahydrate; and H. Perlberger reported a *heptahydrate;* A. Mazzucchelli and G. Zangrilli obtained the *heptadecahydrate* by concentrating a soln. of ammonium hydrophosphate in a little water, mixed with ammonium molybdate, and hydrogen dioxide. F. A. Zenker, and O. W. Gibbs said that the crystals are triclinic prisms which are stable in dry air, but become opaque in moist air. The salt is then no longer soluble in water. The salt is freely soluble in hot water, but less soluble in cold water. The aq. soln. has an acid reaction, and when the aq. soln. is boiled or allowed to stand exposed to air, ammonia is given off, and a white precipitate is formed. O. W. Gibbs reported white or colourless crystals of **ammonium trihydrophosphatohemipentamolybdate,** $(NH_4)_5H_3[P_2O_4(MoO_4)_5].2H_2O$, to be formed by cooling a hot soln. of molybdenum trioxide in one of ammonium phosphate; and also the *tetrahydrate* by neutralizing phosphoric acid with ammonia, adding ammonium paramolybdate; on evaporation, there is formed a gum-like mass which yields white or colourless plates easily soluble in water. H. Perlberger also prepared the *hexahydrate.* J. Meschoirer also prepared the dihydrate; and H. Perlberger, A. Arnfeld, and J. Meschoirer reported a *hemitridecahydrate*, and H. Perlberger, a *hexahydrate*. F. Ephraim and M. Brand prepared a complex of a mol of **lithium dihydrophosphatohemipentamolybdate,** $Li_6H_2[P_2O_4(MoO_4)_5]$, and 6 mols of lithium phosphate from a soln. of 3 mols of lithium molybdate, 2 mols of molybdenum trioxide, and a mol of phosphorus pentoxide in water. They also obtained the salt $3Li_2O.P_2O_5.5MoO_3$, with 16 and $17H_2O$. H. Debray prepared **sodium dihydrophosphatohemipentamolybdate,** $Na_6H_2[P_2O_4(MoO_4)_5].13H_2O$, as in the case of the potassium salt. H. Dufet said that the crystals are rhombic bipyramids with the axial ratios $a:b:c$ $=0·7966:1:1·0726$; the (102)-cleavage is complete; the optical character is negative. For Li-, Na-, and Tl-light, at 20°, the optic axial angle, $2V$, is respectively 51° 16′, 51° 18·5′, and 51° 16′; and $2E$, respectively, 90° 2′, 90° 35′, and 90° 58′, while the indices of refraction are, respectively, $\alpha=1·5906$, 1·5962, and 1·6017; $\beta=1·6328$, 1·6411, and 1·6494; and $\gamma=1·6420$, 1·6520, and 1·6610. A rise of temp. of 1° makes the angle $2E$ about 10′ smaller. F. Ephraim and H. Herschfinkel could not prepare **rubidium phosphatohemipentamolybdate.** O. W. Gibbs found that copper sulphate gave no precipitate with a soln. of ammonium phosphatohemipentamolybdate; H. Perlberger obtained **copper phosphatohemipentamolybdate,** $3CuO.P_2O_5.5MoO_3$, by the method used by A. Arnfeld for the manganese and cobalt salts. He also obtained **ammonium copper phosphatohemipentamolybdate,** $3\{(NH_4)_2.Cu\}O_2.P_2O_5.5MoO_3.3H_2O$, by mixing aq. soln. of ammonium and copper phosphatomolybdates; likewise also by the addition of potassium chloride, **potassium copper phosphatohemipentamolybdate,** $3K_2O.CuO.2P_2O_5.10MoO_3.18H_2O$, was obtained. H. Debray reported **silver phosphatohemipentamolybdate,** $3Ag_2O.P_2O_5.5MoO_3.5H_2O$, to be formed by the action of alkali hydroxide or carbonate on silver phosphatodecamolybdate. The colourless crystals are soluble in water. C. Friedheim prepared crystals of **potassium calcium phosphatohemipentamolybdate,** $3K_2O.2CaO.2P_2O_5.10MoO_3.22H_2O$, from soln. of calcium chloride and potassium phosphatohemidecamolybdate. H. Perlberger prepared **cadmium phosphatohemipentamolybdate,** $3CdO.P_2O_5.5MoO_3.5H_2O$, as in the case of the copper salt. O. W. Gibbs obtained **mercurous phosphatohemipentamolybdate** by the action of mercurous nitrate on the ammonium salt.

A. Arnfeld prepared **manganese phosphatohemipentamolybdate,** $3MnO.P_2O_5.5MoO_3.20H_2O$, or $Mn_3H_2[P_2O_4(MoO_4)_5].19H_2O$, by allowing 9 grms. of freshly precipitated manganese hydrophosphate and 18 grms. of molybdenum trioxide to stand in cold water for 14 days. The filtered liquid is evaporated to a syrupy consistency, and treated with alcohol. The yellow, microcrystalline powder, loses 16 mols of water at 90°, and another mol at 100°; all the water is expelled at 150°. The salt is easily soluble in water, and sparingly soluble in alcohol. The aq. soln. gives a precipitate with ammonium or potassium chloride. If a soln. of a mol of ammonium phosphatohemipentamolybdate is treated with 10 mols of manganous chloride, and evaporated over sulphuric acid, crystals of **ammonium manganous phosphatohemipentamolybdate,** $(NH_4)_8MnH_2[P_2O_4(MoO_4)_5]_2.12H_2O$, are formed. A cold soln. of a mol of ammonium phosphatohemipentamolybdate and a mol of manganous chloride gives microscopic needles of **ammonium manganous dihydrophosphatohemipentamolybdate,** $(NH_4)_2Mn_2H_2[P_2O_4(MoO_4)_5].19H_2O$. A soln. of a mol of potassium phosphatohemipentamolybdate and 10 mols of manganous chloride gives **potassium manganous phosphatohemipentamolybdate,** $K_6Mn_2H_2[P_2O_4(MoO_4)_5]_2.29H_2O$, as a yellow, microcrystalline powder, Attempts to prepare **ferric phosphatohemipentamolybdate,** $Fe_2O_3.P_2O_5.5MoO_3.nH_2O$, gave a product of variable composition. The group $[P_2O_4(MoO_4)_5]$ has a basicity of 8, and $[P_2O_4(MoO_4)_5]_2$ has a basicity of 12.

A. Arnfeld obtained **cobaltous phosphatohemipentamolybdate,** $Co_3H_2[P_2O_4(MoO_4)_5].15\frac{1}{2}$ or $16\frac{1}{2}H_2O$, as in the case of the manganese salt; or by evaporating a dil. soln. of a mol of phosphoric acid, 5 mols of molybdenum trioxide, and the theoretical quantity of cobalt carbonate; or by the action of a mol of cobaltous phosphate on 10 mols of molybdenum trioxide suspended in water. The brownish-red crystalline mass is extremely soluble in water, and the soln. with alcohol precipitates an oily liquid which soon crystallizes. If a mol of ammonium phosphatohemipentamolybdate be treated with a soln. of 3 mols of cobaltous chloride in hot water, **ammonium cobaltous dihydrophosphatohemipentamolybdate,** $(NH_4)_2Co_2H_2[P_2O_4(MoO_4)_5].9H_2O$, separates out on cooling as a brick-red, microcrystalline precipitate which is decomposed by water. A soln. containing a mol of ammonium phosphatohemipentamolybdate and 10 mols of cobaltous chloride furnishes rose-coloured crystals of **ammonium cobaltous phosphatohemipentamolybdate,** $(NH_4)_8CoH_2[P_2O_4(MoO_4)_5]_2.11H_2O$, when evaporated over sulphuric acid. The salt is sparingly soluble in cold water. The corresponding potassium salts —**potassium cobaltous dihydrophosphatohemipentamolybdate,** $K_2Co_2H_2[P_2O_4(MoO_4)_5].14H_2O$, and **potassium cobaltous phosphatohemipentamolybdate,** $K_8CoH_2[P_2O_4(MoO_4)_5]_2.11H_2O$—were obtained by analogous processes.

A. Arnfeld prepared **nickel phosphatohemipentamolybdate,** $Ni_3H_2[P_2O_4(MoO_4)_5].19H_2O$, by boiling a mol of freshly-prepared nickel phosphate, and 5 mols of molybdenum trioxide with water, evaporating the green soln. to a syrupy consistency, and adding alcohol. The oily liquid crystallizes over phosphorus pentoxide. The green needles are decomposed by cold water. Green crystals of **ammonium nickel dihydrophosphatohemipentamolybdate,** $(NH_4)_6Ni_2H_2[P_2O_4(MoO_4)_5].9H_2O$, and of **ammonium nickel phosphatohemipentamolybdate,** $(NH_4)_8NiH_2[P_2O_4(MoO_4)_5]_2.11H_2O$, as well as of **potassium nickel dihydrophosphatohemipentamolybdate,** $K_2Ni_2H_2[P_2O_4(MoO_4)_5].12H_2O$, and **potassium nickel phosphatohemipentamolybdate,** $K_8NiH_2[P_2O_4(MoO_4)_5]_2.11H_2O$, were obtained as in the case of the corresponding cobaltous salts.

F. Ephraim and H. Herschfinkel reported *rubidium phosphatotetritaenneamolybdate,* $5Rb_2O.2P_2O_5.9MoO_3.13H_2O$, as a white, crystalline powder, from a soln. of a mol of rubidium carbonate and 0·5 mol of phosphorus pentoxide boiled with a mol of molybdenum trioxide. The filtered soln. is concentrated by evaporation and allowed to stand for crystallization. H. Perlberger prepared *ammonium cadmium phosphatotetritaenneamolybdate,* $3(NH_4)_2O.2CdO.2P_2O_5.9MoO_3.14H_2O$, by the action of cadmium chloride on a soln. of the pentammonium phosphatohemipentamolybdate.

O. W. Gibbs reported *barium phosphatohexitatetradecamolybdate,* $4BaO.3P_2O_5.14MoO_3.55H_2O$, from a soln. of barium hexametaphosphate in ammonium heptamolybdate. If the soln. be treated with mercurous nitrate, a mercury salt is obtained.

O. W. Gibbs also reported *ammonium stannic phosphatohexitetradecamolybdate,* $3(NH_4)_2O.4SnO_2.3P_2O_5.14MoO_3.28H_2O$, to be obtained as a yellow, crystalline precipitate by the action of ammonium chlorostannate on a soln. of an alkali phosphatomolybdate. The product is almost insoluble in boiling water.

C. Friedheim prepared the potassium salt of **phosphatodimolybdic acid,** $H_3[PO_2(MoO_4)_2].nH_2O$. By the interaction of a mol of potassium hydrophosphate and 2 mols of molybdenum trioxide, there are formed hemipentamolybdates and **potassium hydrophosphatodimolybdate,** $K_2H[PO_2(MoO_4)_2].3\frac{1}{2}H_2O$. C. Friedheim, and A. Mazzucchelli and G. Zangrilli also prepared **ammonium hydrophosphatodimolybdate,** $(NH_4)_2H[PO_2(MoO_4)_2].2H_2O$, and the *hemipentahydrate.* F. Ephraim and M. Brand reported lithium **phosphatodimolybdate,** $5Li_2O(P_2O_5.4MoO_3)_2.28H_2O$, to be formed in white needles, from a boiling soln. of 25 grms. of lithium phosphate and 77 grms. of molybdic acid. The salt loses 16 mols. of water at 100°, 18 mols. at 120°, 23 mols. at 145°, and the remainder at a red-heat. H. Perlberger obtained **copper phosphatodimolybdate,** $2CuO.P_2O_5.4MoO_3.19$ or $20H_2O$, by the action of a soln. of molybdic acid and copper oxide on phosphoric acid. A. Arnfeld prepared **cobalt hydrophosphatodimolybdate,** $CoH[PO_2(MoO_4)_2].nH_2O$, as a brown amorphous precipitate, by heating in a sealed tube a mixture of a mol of ammonium phosphatohemipentamolybdate, 3 mols of cobaltous chloride and 25 c.c. of water, and likewise also a green precipitate of **nickel hydrophosphatodimolybdate,** $NiH[PO_2(MoO_4)_2].nH_2O$.

C. Friedheim obtained the potassium salt of **phosphatomolybdic acid,** $H_3[PO_3(MoO_4)].nH_2O$, namely potassium phosphatomolybdate, $KH_2[PO_3(MoO_4)].11H_2O$, from a soln. of a mol of **potassium dihydrophosphatomolybdate,** and a mol of molybdenum trioxide. The salt may be constituted $(HO)_2$–PO–$KMoO_4$. J. Meschoirer also obtained **ammonium dihydrophosphatomolybdate,** $(NH_4)H_2[PO_3(MoO_4)]$.

F. Ephraim and H. Herschfinkel found that the evaporation of the mother-liquid obtained in the preparation of rubidium phosphatotetritaenneamolybdate furnishes *rubidium phosphatohexitadecamolybdate,* $7Rb_2O.3P_2O_5.10MoO_3.15\frac{1}{2}H_2O$.

M. Seligsohn reported *ammonium lead phosphatopentadecamolybdate,* $3(NH_4)_2O.30PbO.P_2O_5.30MoO_3$, to be formed by boiling the lead phosphate with an excess of a soln. of lead acetate. It is a white powder. W. Bodenbinder reported a *calcium lead phosphatomolybdate* to occur in plates, resembling wulfenite, in the plumbocalcite of San Luis, Argentine. Its sp. gr. is over 7.

O. W. Gibbs obtained orange-yellow crystals of *platinum phosphatomolybdate* by dissolving platinic hydroxide in a boiling soln. of sodium phosphatododecamolybdate and evaporating the filtered liquid.

Owing to the ready hydrolysis of pyrophosphoric acid in aq. soln. to form orthophosphoric acid, it is not possible to obtain ammonium and potassium pyrophosphates of a high degree of purity in aq. soln. A. Rosenheim and T. Triantaphyllides prepared **sodium molybdic pyrophosphate,** $Na(MoP_2O_7).12H_2O$, in brown prisms, by adding a soln. of tripotassium molybdic hexachloride to a soln. of sodium pyrophosphate at 80° to 90°. A. Rosenheim and M. Schapiro tried to prepare potassium and ammonium pyrophosphatomolybdates by the use of pyrophosphates instead of the orthophosphates, but the results were unsatisfactory. The products were probably mixtures of ordinary phosphatododecamolybdates with the pyrophosphatomolybdates. By heating a soln. of 12 mols of lithium molybdate, and adding a mol of lithium pyrophosphate, a pale yellow, microcrystalline precipitate of **lithium pyrophosphatododecamolybdate,** $2Li_2O.P_2O_5.12MoO_3.17H_2O$, is produced. The salt forms a yellow soln. with water, and the soln. is decolorized by mineral acids owing to the hydrolysis of the pyrophosphate. A. Rosenheim and M. Schapiro added that *es ist nicht unwahrscheinlich* that the compound is the same as F. Ephraim and M. Brand's $3Li_2O.P_2O_5.12MoO_3.18H_2O$. A boiling soln. of 12 mols of normal sodium molybdate and a mol of sodium pyrophosphate with 24 mols of hydrochloric acid, when cooled deposits pale yellow, microscopic plates of **sodium pyrophosphatododecamolybdate,** $2Na_2O.P_2O_5.12MoO_3.26H_2O$. The yellow, aq. soln. becomes colourless in the presence of hydrochloric acid owing to the hydrolysis of the pyrophosphate to orthophosphate.

According to O. W. Gibbs, if the orange precipitate which ammonia produces in a soln. of sodium gold pyrophosphate be boiled with a soln. of ammonium molybdate, pale yellow *ammonium gold amminophosphatomolybdate,* $24NH_3.12Au_2O_3.7P_2O_5.3MoO_3.21H_2O$, is formed. It explodes when heated. A dark orange-red, crystalline precipitate is produced when a soln. of sodium gold chloride is treated with sodium pyrophosphatomolybdate; and if the precipitate be boiled with a soln. of ammonium molybdate, orange-red crystals of *sodium gold amminophosphatomolybdate,* $Na_2O.5Au_2O_3.15NH_3.2P_2O_5.11MoO_3.10H_2O$, are formed. The salt explodes when heated; it forms a turbid liquid with hot water; and dissolves in hot hydrochloric acid. A soln. of sodium gold pyrophosphate, $AuNaP_2O_7$, boiled with ammonium molybdate gave a buff precipitate of *ammonium sodium gold pyrophosphatohemihenamolybdate,* $15(NH_4)_2O.Na_2O.6Au_2O_3.4P_2O_5.22MoO_3.5H_2O$. It does not explode when heated.

O. W. Gibbs described *ammonium manganous pyrophosphatomolybdate,* $5(NH_4)_2O.10MnO.2P_2O_5.20MoO_3.10H_2O$, as a reddish-yellow, sparingly soluble precipitate, formed by digesting manganous pyrophosphate for some time with a conc. soln. of ammonium paramolybdate. Likewise also *sodium manganous pyrophosphatomolybdate,* $9Na_2O.7MnO.2P_2O_5.22MoO_3.57H_2O$, by the action of manganous chloride on a boiling soln. of sodium pyrophosphate and molybdenum trioxide. The pale red, amorphous precipitate becomes crystalline when allowed to stand under its mother-liquor. When crystallized from hot water, it forms sulphur-yellow crystals. It is sparingly soluble in cold water, and fairly soluble in hot water.

G. Denigès [3] obtained sapphire-blue, hexagonal plates of a **molybdosic phosphate,** $[4MoO_3.MoO_2]_2H_3PO_4.4H_2O$, from a soln. of sodium molybdate and sodium hydrophosphate. A. Verda said that the product is obtained only when tin or aluminium is present, and that the blue product is soluble in ether.

REFERENCES.

[1] W. Wardlaw and R. L. Wormell, *Journ. Chem. Soc.*, 1087, 1927; G. Saring, *Versuche über den Aufschluss von Phosphaten durch Kieselsaure bei hohen Temperaturen*, Dresden, 1906; A. Colani, *Compt. Rend.*, **165**. 185, 1917; L. Malaprade, *Ann. Chim. Phys.*, (10), **9**. 104, 159, 1929; G. Denigès, *Bull. Soc. Pharm., Bordeaux*, **65**. 107, 1927; A. Verda, *Pharm. Acta Helvetica*, **3**. 4, 1928; F. de Carli, *Atti Congres. Chim. Pure Appl.*, 1151, 1926; A. S. Schachoff, *Trans. Russ. Inst. Chem. Reagents*, **4**. 74, 1927.

[2] J. J. Berzelius, *Schweigger's Journ.*, **22**. 51, 1817; *Ann. Chim. Phys.*, (2), **17**. 5, 1921; *Pogg. Ann.*, **4**. 153, 1825; **6**. 331, 369, 1826; **7**. 261, 1826; L. F. Svanberg and H. Struve, *Svenska Akad. Handl.*, **1**. 9, 1848; *Journ. prakt. Chem.*, (1), **44**. 257, 1848; *Phil. Mag.*, (3), **33**. 409, 524, 1848; H. Struve, *Journ. prakt. Chem.*, (1), **54**. 288, 1851: E. Drechsel, *Ber.*, **20**. 1452, 1887; A. S. Schachoff, *Trans. Russ. Inst. Chem. Reagents*, **4**. 74, 1927; A. Verda, *Chem. Ztg.*, **30**. 329, 1906; *Contributions à l'étude de l'acide phosphatomolybdique*, Locarno, 1905; O. T. Christensen, *Journ. prakt. Chem.*, (2), **23**. 26, 1881; L. Gmelin, *ib.*, (1), **67**. 408, 1856; V. Eggertz, *ib.*, (1), **79**. 496, 1860; M. Seligsohn, *Disseratio de acidi phosphoricomolybdici in nonnullas bases actione*, Berolini, 1856; *Journ. prakt. Chem.*, (1), **67**. 470, 1856; F. A. Zenker, *ib.*, (1), **58**. 256, 1853; F. L. Sonnenschein, *ib.*, (1), **53**. 342, 1851; (1), **56**. 302, 1852; *Liebig's Ann.*, **104**. 45. 1857; T. Salzer, *ib.*, **187**. 322, 1877; E. Péchard, *Compt. Rend.*, **109**. 301, 1889; F. Parmentier, *ib.*, **104**. 686, 1887; H. Debray, *ib.*, **46**. 1098, 1858; **66**. 704, 1868; *Bull. Soc. Chim.*, (2), **5**. 404, 1866; H. Beuf, *ib.*, (3), **3**. 852, 1890; A. Villiers and F. Borg, *ib.*, (3), **9**. 486, 1893; *Compt. Rend.*, **116**. 989, 1893; A. Laurent, *ib.*, **31**. 692, 1850; S. Posternak, *ib.*, **170**. 930, 1920; R. Finkener, *Ber.*, **11**. 1638, 1878; *Dingler's Journ.*, **230**. 190, 1878; A. Miolati and R. Pizzighelli, *Journ. prakt. Chem.*, (2), **77**. 417, 1908; A. Miolati, *Rivista Tecnica*, **3**. 385, 1903; *Gazz. Chim. Ital.*, **33**. ii, 335, 1903; M. G. Levi and E. Spelta, *ib.*, **33**. i, 207, 1903; A. Mazzucchelli and G. Zangrilli, *ib.*, **40**. ii, 55, 1910; *Atti Accad. Lincei*, (5), **18**. ii, 259, 1909; O. W. Gibbs, *Amer. Chem. Journ.*, **3**. 317, 1881; **17**. 167, 1895; *Proc. Amer. Acad.*, **16**. 109, 127, 1881; **17**. 62, 1882; **18**. 233, 1883; **21**. 50, 116, 1886; *Ber.*, **10**. 1385, 1877; *Amer. Journ. Science*, (3), **14**. 62, 1877; F. Kehrmann, *Ber.*, **20**. 1811, 1887; F. Kehrmann and E. Böhm, *Zeit. anorg. Chem.*, **7**. 406, 1894; C. Friedheim, *ib.*, **6**. 33, 1894; F. Hundeshagen, *Zeit. anal. Chem.*, **28**. 141, 1889; *Chem. News*, **60**. 168, 177, 188, 201, 215, 1889; A. König, *Landw. Versuchsstät.*, **26**. 360, 1881; *Zeit. anal. Chem.*, **10**. 307, 1871; E. Richter, *ib.*, **10**. 471, 1871; C. R. Fresenius, *ib.*, **3**. 446, 1864; A. Werncke, *ib.*, **14**. 12, 1875; H. C. Babbitt, *Journ. Anal. Appl. Chem.*, **7**. 165, 1893; E. Spiess, *Viertelj. prakt. Pharm.*, **9**. 257, 1860; M. Nutzinger, *ib.*, **4**. 549, 1855; A. von Lipowitz, *Pogg. Ann.*, **109**. 135, 1860; H. Rose, *ib.*, **76**. 26, 1847; C. F. Rammelsberg, *Sitzber. Akad. Berlin*, 573, 1877; *Ber.*, **10**. 1776, 1877; H. Dufet, *Bull. Soc. Min.*, **24**. 118, 1901; A. E. Nordenskjöld, *Svenska Akad. Handl.*, 1, 1874; G. Pohl, *Beiträge zur Kenntnis einiger Verbindungen des Molybdäns und deren Untersuchungen*, Bern, 1906; F. Elias, *Beiträge zur Kenntnis der gelben Phosphormolybdate*, Bern, 1906; L. Duparc and F. Pearce, *Bull. Soc. Min.*, **18**. 39, 1895; E. Brauer, *Ueber die Beständigkeit der Anionen der Heteropolysäuren*, Berlin, 1918; A. Rosenheim and E. Brauer, *Zeit. anorg. Chem.*, **93**. 284, 1915; A. Rosenheim and T. Triantaphyllides, *Ber.*, **48**. 582, 1915; A. Rosenheim, *Zeit. Elektrochem.*, **17**. 689, 1911; A. Rosenheim and A. Bertheim, *Zeit. Elektrochem.*, **17**. 689, 1911; *Zeit. anorg. Chem.*, **34**. 427, 1903; A. Rosenheim and J. Pinsker, *ib.*, **70**. 77, 1911; A. Rosenheim and A. Traube, *ib.*, **91**. 96, 1915; A. Rosenheim and J. Jaenicke, *ib.*, **101**. 247, 1917; A. Arnfeld, *Beiträge zur Kenntnis der Phosphormolybdate*, Berlin, 1898; C. Friedheim, *Zeit. anorg. Chem.*, **4**. 275, 1893; C. Friedheim and J. Meschoirer, *ib.*, **6**. 83, 1894; J. Meschoirer, *Ueber Arsenomolybdate und Phosphormolybdate des Ammoniums*, Berlin, 1894; H. Perlberger, *Ueber Kupfer und Cadmium Phosphormolybdate*, Bern, 1904; C. Friedheim and G. Wirtz, *Zeit. anorg. Chem.*, **4**. 288, 1893; G. Wirtz, *Die Einwirkung der Molybdänsäure auf die Phosphate des Kaliums und Natriums; ein Beitrag zur Kenntnis der sogennanten phosphormolybdänsauren Salze*, Berlin, 1892; F. A. McDermott, *Journ. Amer. Chem. Soc.*, **33**. 410, 1911; F. Ephraim and H. Herschfinkel, *Zeit. anorg. Chem.*, **65**. 233, 1909; H. Herschfinkel, *Ueber Molybdate, Sulfomolybdate Phosphor- und Arsenomolybdate des Rubidiums und Cæsiums*, Bern, 1907; M. Brand, *Ueber Molybdate, Sulfomolybdate, und Phosphormolybdate des Lithiums*, Bern, 1905; F. Ephraim and M. Brand, *Zeit. anorg. Chem.*, **64**. 261, 1909; W. Bodenbinder, *Zeit. prakt. Geol.*, **9**. 52, 1901; M. Schapiro, *Ueber Heteropolymolybdänate der Phosphorigensäure, Pyrophosphorsäure, und Arsenigensäure*, Berlin, 1923; A. Rosenheim and M. Schapiro, *Zeit. anorg. Chem.*, **129**. 196, 1923; T. G. y Arnal, *Anal. Soc. Fis. Quim.*, **26**. 435, 1928; F. Feigl, *Zeit. anal. Chem.*, **74**. 386, 1929; H. von Jüptner, *Fortschritte in Eisenhüttenlaboratorien*, Leipzig, 1896; A. von Endredy, *Zeit. anorg. Chem.*, **194**. 239, 1930; H. Seligson, *Arch. Pharm.*, **268**. 147, 1930; L. Malaprade, *Bull. Soc. Chim.*, (4), **39**. 325, 1926.

[3] G. Denigès, *Compt. Rend.*, **184**. 687, 1927; *Pharm. Acta Helvetica*, **3**. 52, 1928; A. Verda, *ib.*, **3**. 4, 56, 1928.

CHAPTER LXII

TUNGSTEN

§ 1. The History of Tungsten

THE history of tungsten is closely associated with a mineral which was thought to contain tin, presumably because of its density. Thus, J. G. Wallerius [1] called the mineral from Bohemia *lapides stanniferi spathacei;* C. von Linnæus, *stannum spathosum subdiaphanum album;* and A. F. Cronstedt, *ferrum calciforme, terra quadam incognita intime mixtum.* In Sweden, the mineral was called tungsten—from the Swedish *tung*, heavy or ponderous; and *sten*, stone—and A. G. Werner called it *Schwerstein.*

G. Agricola also referred to another brownish-black mineral which he called *lupi spuma*, or *lapis niger ex quo conflatur candidum plumbum* (tin); J. G. Wallerius called it *volfram*, and regarded it as *ferrum arsenico mineralisatum;* while A. F. Cronstedt called it *wolfram*, and added that it contains *magnesia* (*i.e.* Mn) *parva cum portione martis et jovis mixta.* It was also called *lupis jovis* in allusion to its weight. R. J. Haüy called the mineral *scheelin ferruginê;* and A. Breithaupt, **wolframite,** the name which it now bears. This mineral was described by L. Ercker, P. Albinus, A. von Schönberg, B. Rossler, J. A. Cramer, J. F. Henckel, S. Rinman, etc. G. Agricola suggested that the term wolfram comes from the German word " wolf," and " *ram* " or *rahm*, froth; hence his Latin term *lupi spuma* for wolfram. Others deny this derivation and say that the term is of unknown origin. According to A. Gurlt, and W. Pryce, the tin miners of Saxony and Bohemia called it *wolf, wolfart, wolfort, wolfrig*, and *wolffert* (A. von Schönberg), *i.e.* the *wolfish* or *devouring ore*, in allusion—as stated by A. Rössing, and others—to the low yield of tin obtained from tin ores associated with this mineral. The ore was also called *woolfram* (J. A. Cramer), and *wolferam* (L. Ercker). *Lupus*, or *wolf*, was one of the alchemist's terms for antimony (*q.v.*); and G. Agricola's term *lupus spuma* is now understood to mean that the mineral was mistaken for an antimony ore. The *spuma* is probably an allusion to the scum formed when, say, gold is purified by melting it with antimony. According to T. Blair, the termination *ram* has a similar signification to that of *spuma*—a term applied by the Germans to substances with a laminated structure. I. Koppel discussed the history of tungsten. The tin miners of Cornwall regarded it as an obnoxious ore because " it eats up tin as a wolf eats up sheep," and they named it *cal* or *call* or *mock-lead.* W. Pryce said:

> In Cornwall, after the tin is separated from all other impurities, there remains a quantity of this mineral substance, *cal*, which, being of equal gravity, cannot be separated from the tin ore by water; therefore this reduces its value down to eight or nine parts of metal for twenty of mineral.

J. F. Henckel said that wolfram is an arsenical and ferruginous ore of tin. J. G. Wallerius, and A. Cronstedt regarded it as a kind of manganese ore containing tin and iron; J. H. G. von Justi, an ore containing iron, arsenic, tin, and an earth which is not metallic—and, added J. W. Baumer, sulphur and calcareous earth; G. A. Scopoli, an ore of tin yielding 28 lbs. per hundredweight; B. G. Sage, a combination of iron and basalt; and J. G. Lehmann, a vitrifiable or glassy earth containing iron and a small proportion of tin. J. G. Kaim supposed wolfram to contain a semi-metal; but the regulus he described is unlike that which is now known to be derived from that ore.

In 1781, C. W. Scheele, in his memoir: *Tungstens beständs-delar*, showed that tungsten ore (scheelite) is a compound of lime with a peculiar acid. He fused the ore with potassium carbonate, dissolved the mass in water, and added nitric acid. The white precipitate was washed and dried. He then showed that the product is the acid of tungsten—a metallic acid in which the metal is reduced by phlogiston to a metallic calx. He demonstrated the other component of the ore to be lime. Hence, the mineral is a calcium tungstate. D. L. G. Karsten then called the mineral *scheelerz;* R. J. Haüy, *scheelin calcaire;* A. Breithaupt, *scheelspath;* and C. C. Leonhard, **scheelite,** the name which the mineral now bears.

T. Bergman said that the acid of tungsten in *lapis ponderosus* is the calx of a metal which has a high sp. gr.; it is precipitated by potassium ferrocyanide, and colours glass. J. J. and F. de Elhuyar, in their *Análisis quimico del volfram y exámen de un nuovo metal que entra en su composicion* (Bascongada, 1783), showed that the mineral wolfram contains the same acid as tungsten ore, but in wolfram, the acid is associated with iron and manganese instead of lime. These chemists obtained the metal by reducing the oxide with carbon; and they described alloys of tungsten with gold, silver, lead, and iron. The question has been raised: Were the Spanish chemists the first to isolate the metal? Actually one at least of the brothers de Elhuyar worked under the direction of C. W. Scheele, and T. Bergman for some years, and, in their memoir, the two brothers—perhaps modestly—made no claim to having been the discoverers of the metal—because, according to J. J. Runner and M. L. Hartmann, C. W. Scheele had probably already prepared the metal. S. Rinman definitely ascribed the discovery of the metal to C. W. Scheele, and stated that its alloy with iron was prepared by J. J. and F. de Elhuyar. In spite of these and similar statements, the fact remains that the first published account of the isolation of the element is that of the Spaniards, J. J. and F. de Elhuyar. In 1785, R. E. Raspe referred to a Cornish mineral, which, when treated with a soln. of stannous chloride gave a blue coloration; and he added that he succeeded in obtaining from it a regulus in the proportion of 36·5 to 37·3 per cent. This regulus was said "to contain very little iron; to be most refractory in the fire; and to cut glass like the most highly tempered steel. It will therefore perhaps be useful in hardening iron and steel for some classes of work." The name J. J. and F. de Elhuyar, by the way, appears in literature spelt in many ways. According to R. A. Hadfield, on the authority of the Royal Library, Madrid, the spelling is "de Elhuyar," not d'Elhujar, etc. J. J. and F. de Elhuyar called the elemental metal *wolfram* or tungsten. The metal came to be called *scheelium,* and J. J. Berzelius suggested *wolframium* because "C. W. Scheele had already immortalized his name by other great discoveries to such an extent as to preclude the necessity of its being handed down to posterity by the denomination of a substance." The term *wolfram* is used for the metal in Germany; *tungsten* in England; and *tungstène* in France. The symbol W is in fairly general use, although in France and Italy Tu is sometimes employed. E. Moles [2] argued in favour of the term wolfram. The metal was also prepared by reducing the oxide by carbon by A. Ruprecht, L. N. Vauquelin and L. Hecht, W. Allen and A. Aiken, C. F. Bucholz, and J. J. Berzelius.

M. Gerber [3] stated that tungsten is not a simple substance but is accompanied by another element to which he gave the name *neotungsten,* and the latter is estimated to have the at. wt. 188. He said that soluble metatungstic acid furnishes ammonium isotungstate, described by A. Laurent. In the isotungstic acid prepared from this salt, the metal had an at. wt. ranging from 186·5 to 187—ordinary tungsten has the at. wt. 184. It is assumed that the isotungstic acid contained neotungsten. These statements have not been confirmed—*vide* neomolybdenum—P. Barbe could find no evidence of the existence of isotungstates, and never obtained a specimen with a mol. wt. higher than usual. He said that the ammonium isotungstate of M. Gerber was ammonium sodium tungstate.

There are a few books, monographs, and memoirs on the general properties, etc., of tungsten—*e.g.*

J. J. Runner and M. L. Hartmann, *The Occurrence, Chemistry, Metallurgy, and Uses of Tungsten*, Rapid City, 1918 ; M. L. Hartmann, *A Bibliography of Tungsten*, Rapid City, 1918 ; *Pahasapa Quart.*, **5.** 2, 1916 ; A. Joly, *Tungstène*, Paris, 1888 ; P. Truchot, *Les terres rares*, Paris, 1904 ; J. C. Escard, *Les métaux spéciaux*, Paris, 1910 ; C. Baskerville, *Eng. Min. Journ.*, **87**, 203, 1909 ; *Met. Chem. Engg.*, **11.** 319, 1913 ; J. Castner, *Stahl Eisen*, **16.** 517, 1896 ; J. Ohly, *The Rare Metals*, London, 1905 ; H. Dickinson, *Min. Science*, **57.** 123, 1908 ; H. F. Baumhauser, *Bayer. Ind. Gewerbebl.*, 141, 1912 ; *L'Industria*, **26.** 414, 1912 ; *Ind. Chim.*, **12.** 343, 1912 ; A. Haenig, *Oesterr. Zeit. Berg. Hütt.*, **56.** 177, 1908 ; E. C. Reibe, *Min. World*, **26.** 565, 1907 ; A. B. Frenzel, *Min. Science*, **65.** 73, 1912 ; O. J. Steinhart, *Min. Scient. Press.*, **109.** 64, 1914 ; H. Fleck, *Addresses on the Rare Metals*, New York, 1915 ; A. C. Rubel, *Bull. Arizona State Bur. Mines*, 11, 1916 ; H. W. Hutchins, *Min. Mag.*, **17.** 39, 85, 1917 ; C. J. Smithells, *Tungsten*, London, 1926 ; H. Leiser, *Wolfram*, Halle a. S., 1910 ; *Chem. Ztg.*, **35.** 665, 1911 ; H. Mennicke, *Die Metallurgie des Wolframs*, Berlin, 1911 ; N. Branoic, *Giorn. Bibliogr. Tech. Internat.*, **1.** 3, 1925 ; J. L. F. Vogel, *Chem. Age*, **3.** 306, 1920 ; L. Moser, *Oesterr. Chem. Ztg.*, **26.** 67, 1923 ; C. Matignon, *Chim. Ind.*, **3.** 277, 1920 ; G. Aichino, *Il Tungsteno*, Tunis, 1916 ; P. Nicolardot, *Rev. Mét.*, **5.** 9, 1908.

REFERENCES.

[1] J. G. Wallerius, *Mineralogia*, Stockholm, 268, 303, 1747 ; A. G. Werner, *Berg. Journ.*, 386, 1789 ; A. F. Cronstedt, *Akad. Handl. Stockholm*, **21.** 227, 1751 ; *Försök till Mineralogie eller Mineral Rikets Upställning*, Stockholm, 107, 183, 1758 ; C. von Linnæus, *Systema naturæ*, Lugduni Batavorum, 1768 ; D. L. G. Karsten, *Mineralogische Tabellen*, Berlin, 56, 1800 ; R. J. Haüy, *Traité de minéralogie*, Paris, **4.** 311, 1801 ; A. Breithaupt, *Kurze Charakteristik des Mineralsystems*, Freiberg, 23, 1820 ; *Vollständige Charakteristik des Mineralsystems*, Dresden, 227, 1832 ; C. C. Leonhard, *Handbuch der Oryktognosie*, Heidelberg, 594, 1821 ; J. G. Lehmann, *Probierkunst*, Berlin, 1761 ; J. G. Kaim, *Dissertatio inauguralis chemica de metallis dubiis*, Viennæ, 1770 ; J. J. and F. de Elhuyar, *Análisis quimico del volfram y exámen de un nuovo metal que entra en su composicion*, Bascongada, 1783 ; *A Chemical Examination of Wolfram and Examination of a New Metal which enters into its Composition*, London, 1785 ; *Chemische Zerkliederung des Wolframs*, Halle, 1786 ; *Mém. Acad. Toulouse*, **2.** 141, 1784 ; C. W. Scheele, *Akad. Handl. Stockholm*, **2.** 89, 1781 ; *Journ. Phys.*, **22.** 724, 1783 ; J. J. Berzelius, *Schweigger's Journ.*, **16.** 476, 1816 ; *Pogg. Ann.*, **4.** 147, 1825 ; **8.** 267, 1826 ; *Ann. Chim. Phys.*, (2), **17.** 13, 1821 ; T. Bergman, *Sciagraphia regni mineralis*, Leipzig, 1782 ; London, 47, 1783 ; G. Agricola, *De natura fossilium*, Basiliæ, 255, 1546 ; A. Gurlt, *Trans. Amer. Inst. Min. Eng.*, **22.** 236, 1893 ; R. A. Hadfield, *Journ. Iron. Steel Inst.*, **64.** ii, 22, 1903 ; I. Koppel, *Chem. Ztg.*, **50.** 969, 1926 ; L. Ercker, *Fleta minor*, Prag, 1574 ; London, 1883 ; P. Albinus, *Meissnische Land- und Bergchronik*, Wittenberg, 1580 ; Dresden, 1590 ; B. Rossler, *Speculum metallurgiæ politissimum*, Dresden, 148, 1700 ; J. A. Cramer, *Elementa artis decimasticæ*, Leyden, 1739 ; London, 1741 ; J. F. Henckel, *Pyritologie*, London, 1757 ; S. Rinman, *Försök till Jernets Historia*, Stockholm, 1782 ; Berlin, **2.** 216, 1815 ; W. Pryce, *Mineralogia cornubiensis*, London, 1778 ; A. von Schön, berg, *Berginformation*, Leipzig, 109, 1693 ; J. J. Runner and M. L. Hartmann, *The Occurrence, Chemistry, Metallurgy and Uses of Tungsten*, Rapid City, South Dakota, 1918 ; T. Blair, *Chromium and Tungsten and their Alloys with Iron*, Sheffield, 1894 ; A. Rössing, *Geschicht der Metalle*, Berlin, 248, 1901 ; J. H. G. von Justi, *Grundriss der gesammten Mineralogie*, Göttingen, 1757 ; J. W. Baumer, *Historia naturalis regni mineralogici*, Francofurti, 1780 ; G. A. Scopoli, *Principia Mineralogiæ systematicæ et practicæ*, Prague, 1772 ; B. G. Sage, *Élémens de minéralogie docimastique*, Paris, 1777 ; R. E. Raspe, *Crell's Ann.*, i, 546, 1785 ; *Reise durch England in Rücksicht auf Manufacturen*, Berlin, 1785 ; in H. L. Duhamel du Monceau, *Encyclopedie methodique*, Paris, **1.** 330, 1786.

[2] A. Ruprecht, *Ann. Chim. Phys.*, (1), **8.** 3, 1791 ; *Journ. Phys.*, **37.** 230, 1790 ; L. N. Vauquelin and L. Hecht, *Journ. Mines*, **4.** 19, 1796 ; C. F. Bucholz, *Schweigger's Journ.*, **3.** 1, 1811 ; J. J. Berzelius, *ib.*, **16.** 476, 1816 ; *Ann. Chim. Phys.*, (2), **17.** 13, 1825 ; *Pogg. Ann.*, **4.** 147, 1825 ; **8.** 267, 1826 ; W. Allen and A. Aiken, in A. and C. R. Aiken, *Dictionary of Chemistry*, London, **2.** 445, 1807 ; E. Moles, *Anal. Espan. Fis. Quim.*, **26.** 234, 1928.

[3] M. Gerber, *Monit. Scient.*, (5), **7.** 73, 121, 169, 219, 1917 ; P. Barbe, *ib.*, (5), **9.** 73, 1919 ; A. Laurent, *Ann. Chim. Phys.*, (3), **21.** 54, 1847.

§ 2. The Occurrence of Tungsten

Tungsten does not occur in the elemental form in nature. Its compounds are among the scarcer constituents of the earth's crust. According to F. W. Clarke and H. S. Washington,[1] the average proportion of tungsten in the igneous rocks of the earth's crust is 5×10^{-5} per cent. J. H. L. Vogt estimated $n \times 10^{-8}$ per cent. W. Vernadsky gave 0·000048 for the percentage amount, and 0·0005 for the atomic proportion. W. and J. Noddack and O. Berg gave 5×10^7 for the absolute abundance of molybdenum in the earth. The general subject was discussed by H. S. Washington, G. Tammann, V. M. Goldschmidt, E. Herlinger, A. von Antropoff, O. Hahn, R. A. Sonder, and J. Joly. H. A. Rowland,[2] and M. N. Saha classed tungsten with the elements whose presence in the sun is doubtful.

The more important tungsten minerals are the wolfram group consisting of iron and manganese tungstates, and the scheelite group consisting of calcium tungstate. They occur irregularly and the lodes are more or less sporadic. The genesis of the ores has been discussed by R. H. Rastall.[3] The ores can be divided into primary and secondary. The primary group includes occurrences in lodes, veins, dykes, and contact deposits; while the secondary group includes alluvial and residual deposits. The primary ores are generally associated with granites, and are often accompanied by tin. The tungsten appears to have been concentrated in the later stages of the solidification of the granite magma to the margin of the intrusion. The wolfram is normally disseminated in the granite, or concentrated in pegmatites, dykes, and quartz veins of direct igneous origin. It also occurs in the country rock adjoining the veins; and some lodes are zones of rock impregnated with ores derived from vapours or solutions passing through cracks due to contraction or faulting. The tungsten in this respect resembles tin, but the tungsten zone has been carried further than the tin. Vapours escaping from the hot interior coming in contact with calcareous rocks formed contact deposits of scheelite. The secondary deposits of tungsten show that in some cases the ore has decomposed, while in other cases the tungsten has resisted weathering influences and accumulated in detrital deposits like tinstone, gold, and platinum.

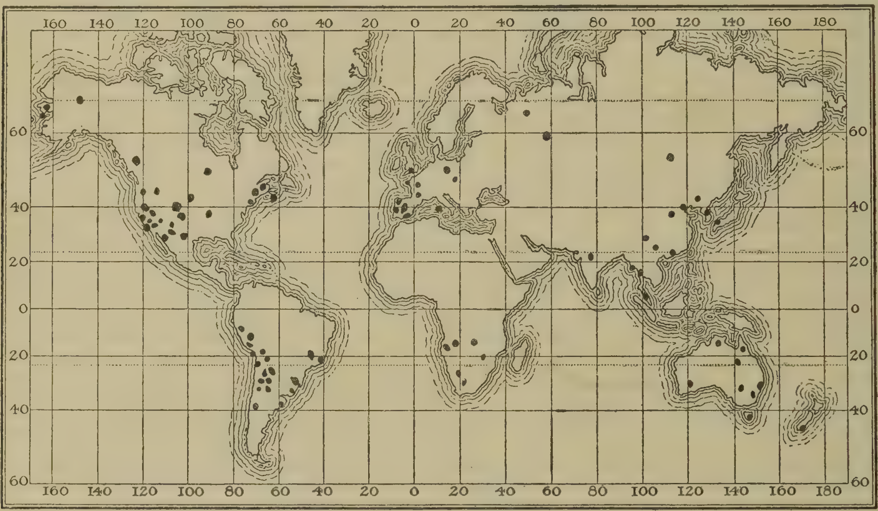


Fig. 1.—The Geographical Distribution of Tungsten Ores.

The geographical distribution of tungsten ores is illustrated by Fig. 1. The main localities are as follow:

Europe.—Nearly all the tungsten ores of the **British Isles**[4] are obtained from Cornwall and the neighbouring parts of Devonshire. The districts are Land's End; Camborne and Redruth; St. Austell; Bodmin Moor; and Callington and Tavistock. The tungsten ore occurring at Carrock Fell, Cumberland, was described by A. M. Finlayson. In **France,**[5] tungsten ores are found in Brittany—at Montbelleux, and Villeray; at Puy-les-Vignes, Haute Vienne; near Chanteloube, Mazataud, and Chabanne; at Meymac; Charente, Saône et Loir, Nievre, and Allier; Framont, Vosges; and St. Lary, Hautes Pyrénées. In **Spain,**[6] there are deposits near Lousame and Cabana, Corunna, Carbia, Pontevedra; Silleda; Zamora; Barrvecotardo, Salamanca; Caceres; Badajos near Jerez de los

Caballeros; Valle de la Serrana; Cordoba and Jaen—Conquista, Malaga, and Paterna. Most of the Spanish output comes from Badajos. In **Portugal,**[7] the northern half of the country is the largest producer of wolfram ores in Europe. There are deposits at Borralha, Serra das Alturas; Braganca, Iffanes, Para, Paradinha, Válle de Seixo, Coelhoso, Mirandella, Miranda do Douro, Sierra da Estrella, Serra de las Mesas; Panasqueira, Silvares; Fundas, Sabugal, Matta da Reinha, Pinhel, Sac Cosmado, Moirmenta, Paredes, Arouca, Capela do Senhor dos Alfitos; Vizeu, and Serra da Estralla. In **Italy,**[8] scheelite occurs in Cagliari, Sardinia, and at Suergiu, and Genna-Gureu. In **Switzerland,**[9] it occurs at Etzlithal. In **Austria-Hungary,** and **Bohemia,**[10] deposits occur near Graupen, Bohemia, and this is a continuation of the Zinnwald-Altenberg field. Deposits also occur at Felsöbanya. In **Russia,**[11] a few deposits of tungsten ore are known—*e.g.* at Baevka, Perm; Nerchinsk, Siberia; and at Pitkäranta, Finland. In **Germany,**[12] wolfram occurs in the tin district of the Erzgebirge, Saxony; Altenberg, and Zinnwald, Saxony; Annaberg, Johanngeorgenstadt, Eibenstock, Neudorf, Tirpersdorf, and Schmiedelfeld. In **Sweden,**[13] a few deposits have been reported, and so also in **Greenland.**[14]

Asia.—In **India,**[15] wolfram occurs at Argagon, Nagpur; Hazaribagh, Bengal; and Degana, Marwar. In **Burma,**[16] a considerable amount of ore is produced in the Tavoy district, Tenasserim; and there are deposits in the Southern Shan States; and in the Thaton district, Lower Burma. In the **Malay States,**[17] and the Straits Settlements extending into the Dutch territory Banka and Billiton, the chief producing states are Perak, Selangor, Negri Sembilan, Pahang, Kedah, and Trengganu. In **Siam,**[18] ore is mined in Nakawn Sritamarat, Trang, and Lacon; and also at Tonkin.

In **Japan,**[19] there are mines in Yamaguchi Ken, Ibaraki Ken, Corea, and Chin Chow, Manchuria. In **China,**[20] tungsten is obtained from the alluvial deposits in the districts of Kwantung, Hunan, and Hong Kong—Haifeng, Lufeng, Puning, Kityang, Wuhua, and Waichow.

Africa.—Tungsten minerals have been reported from the **Union of South Africa**[21]—*e.g.* at Knils River, Cape Province; the tin fields of Waterberg, and Stavoren, and near Leydsdorp. In **South-West Africa,**[22] there are deposits near Little Karas; Ubib, and Goages in Swakopmund; and in the Erongo Mountains. In **Rhodesia,** there are deposits in numerous localities from Wankie to Umtali, and from Lomagundi to the Limpopo river, Lusoakas, Northern Rhodesia; and at Essexvale, Umzingwane.

Northern America.—In **Canada,**[23] there are tungsten ores in Nova Scotia—Stillwater Brook, Halifax; in New Brunswick—Burnt Hill Brook; in Manitoba—Falcon Lake district in British Columbia—Black Prince Group; near Barkerville and in the Kootenay; and near Mayo, Yukon Territory. In the **United States,** the tungsten ores are mainly confined to the Cordilleran region in the west; and in all the Western States with the exception of Wyoming, but more particularly in the Atolia-Randsburg district of California, and about Bouder in Colorado. There are deposits in Alaska,[24] Arizona,[25] California,[26] Colorado,[27] Connecticut,[28] Idaho,[29] Missouri,[30] Montana,[31] Nevada,[32] New Mexico,[33] North Carolina,[34] Oregon,[35] Pennsylvania,[36] South Dakota,[37] Texas,[38] Utah,[39] and Washington.[40] Tungsten has been reported in **Mexico**[41] near Sonora and Durango.

South America.—In **Argentina,**[42] tungsten deposits are mainly confined to the Pampa range—Cajon, Gualapaji, Amboti, Incasti, Colorados, Mazan, Guasapampa, Quines, San Ramon, Pantana, San Ignacio, El Morro, Los Condores, Pisco Yacu, and Cumbre. In **Peru,**[43] the deposits are mainly situated in the department of Ancachs and Libertad on the Pelagatos and Tamboras Mountains. There are deposits in the department of Tayabama; and near Lircay, Huancavelica. In **Chile,**[44] there are deposits in Tacna. In **Bolivia,**[45] there are deposits on the Cordillera Real, and Eastern Cordillera. In **Brazil**[46] deposits occur at Encruzilhada, Rio Grande do Sal; and also in the States of Espirito, Santo, and Minas Geraes.

Australasia.—There are deposits in **Queensland**[47] at Mount Carbine, Wolfram and Bamford. In **New South Wales** they occur in the north-eastern portion and in the west near Broken Hill. There are also the Hill Grove scheelite deposits. In **Victoria,** tungsten is found near Benambra, and near Baragwanatti; at Maldon, and Koetong; in **Tasmania,** near Constable's Creek, Upper Scamander, Gipp's Creek, Storey's Creek, and Moina. Scheelite also occurs on King Island. In **South Australia,** tungsten occurs near Normanville; in **Northern Territory,** in the Pine Creek district, Brock's Wolfram Mine, and Hatches Creek; in **Western Australia,** in the Yalgoo and Murchison fields; and in **New Zealand,**[48] scheelite occurs in the Otago gold-fields, Glenorchy, and Macrae's Flat. Wolfram is reported from Stewart's Island, and the western parts of Nelson.

The valuation of tungsten ores is based on the percentage amount of tungsten trioxide in the conc. ore—65 per cent. is adopted as a standard in Great Britain, while 60 per cent. is preferred in the United States. If the percentage is below the standard, the selling price is penalized. An excessive proportion of phosphorus or arsenic reduces the value of the ore. Before the war, the price was 25*s.* to 35*s.* per unit. In 1915, it was 55*s.* per unit; and in 1918, the price was raised to 60*s.*

with special allowances for losses on high freights and on exchange. The price of chromite ore in 1924 ranged from 86*s*. 3*d*. to 90*s*. 0*d*. per ton. R. H. Rastall and W. H Wilcockson[49] estimated for 1910–1917 the proportion of metal in metric tons in the concentrates produced by different countries to be approximately as follows:

	1910	1913	1917	1924	1929
United Kingdom	278	785	245	2	135
Burma	402	1715	4553	813	2200
Malay States	—	324	1200	430	175
New South Wales	321	173	249	3	68
Queensland	908	549	502	1	45
Tasmania	68	69	245	60	380
New Zealand	145	225	164	3	25
Germany, Austria	60	150	250	83	120
France	30	245	225	—	14
Spain	153	150	800	200	350
Portugal	948	800	1596	400	700
Japan	250	297	1500	10	283
China	—	—	1200	3500	6500
French Indo-China	—	—	—	494	238
Siam	—	281	634	10	35
United States	1652	1395	5006	512	2300
Argentina	1912	539	1000	132	120
Bolivia	207	569	1650	18	585
Peru	12	300	1000	—	100
Mexico	—	—	—	25	45

The tungsten minerals include the wolframite series which, according to F. L. Hess,[50] comprises **ferberite** containing 80 to 100 per cent. $FeWO_4$, and 0 to 20 per cent. $MnWO_4$; **wolframite** with 20 to 80 per cent. $FeWO_4$ and 20 to 80 per cent. of $MnWO_4$; and **hübnerite** with 0 to 20 per cent. $FeWO_4$ and 80 to 100 per cent. $MnWo_4$; **reinite,** $FeWO_4$; there are also **scheelite,** $CaWO_4$; **powellite,** $Ca(Mo,W)O_4$; **stolzite**—tetragonal $PbWO_4$, and **raspite**—monoclinic $PbWO_4$; **chillagite,** a mixture of lead tungstate and molybdate; **cuproscheelite,** or **cuprotungstite,** $CuWO_4.2H_2O$; **tungstite,** or **tungsten ochre,** $WO_3.H_2O$; **ferritungstite,** $Fe_2O_3.WO_3.6H_2O$; and **tungstenite,** WS_2.

H. St. C. Deville[51] found small quantities associated with tantalic acid. F. Zambonini found it in vesbine in crevices in the Vesuvian lava of 1631. M. Mazade detected its presence in the mineral waters of Nérac.

REFERENCES.

[1] F. W. Clarke and H. S. Washington, *Proc. Nat. Acad.*, **8**. 112, 1922; *The Composition of the Earth's Crust*, Washington, 21, 1924; H. S. Washington, *Trans. Amer. Inst. Min. Eng.*, **39**. 735, 1908; *Proc. Nat. Acad.*, **1**. 574, 1915; *Journ. Franklin Inst.*, **190**. 777, 1920; *Bull. Nat. Research Council*, **2**. ii, 30, 1926; *Journ. Washington Acad.*, **14**. 435, 1924; *Amer. Journ. Science*, (4), **38**. 90, 1914; (5), **9**. 351, 1925; (5), **12**. 272, 1926; V. M. Goldschmidt, *Videnskapsselskapets Schrift.*, 11, 1922; 3, 1923; *Zeit. Elektrochem.*, **28**. 411, 1922; *Der Stoffwechsel der Erde*, Kristiania, 1922; G. Tammann, *Zeit. anorg. Chem.*, **131**. 96, 1923; **134**. 269, 1924; E. Herlinger, *Fortschr. Min.*, **12**. 253, 1927; A. von Antropoff, *Sitzber. Nat. Hist. Ver. Rheinlande*, 1, 1926; O. Hahn, *Naturwiss*, **14**. 159, 1926; W. and J. Noddack and O. Berg, *ib.*, **13**. 568, 1925; J. Joly, *The Surface History of the Earth*, Oxford, 1925; J. H. L. Vogt, *Zeit. prakt. Geol.*, **6**. 226, 315, 1898; **7**. 10, 274, 1899; **14**. 223, 1906; W. Vernadsky, *Essai de déscriptive mineralogie*, St. Petersburg, **1**. 121, 740, 1914; *La geochimie*, Paris, 16, 1924; A. E. Fersmann, *Bull. Acad. St. Petersburg*, (6), **6**. 367, 1912; R. A. Sonder, *Zeit. anorg. Chem.*, **192**. 257, 1930.

[2] H. A. Rowland, *Johns Hopkins Univ. Circular*, 85, 1891; *Chem. News*, **63**. 133, 1891; *Amer. Journ. Science*, (3), **41**. 243, 1891; F. E. Baxandall, *Researches on the Chemical Origin of Various Lines in Solar and Stellar Spectra*, London, 1910; M. N. Saha, *Phil. Mag.*, (6), **40**. 808, 1920; R. Wildt, *Zeit. Physik*, **54**. 856, 1929.

[3] R. H. Rastall, *Geol. Mag.*, (6), **5**. 193, 241, 293, 367, 1918; *Min. Journ.*, **122**. 564, 581, 597, 608, 1918; R. H. Rastall and W. H. Wilcockson, *Tungsten Ores*, London, 1920; J. B. Scrivenor, *Tungsten Ores in the Malay Peninsula*, Tavoy, 1916; J. M. Campbell, *Min. Mag.*, **20**. 76, 1919; R. W. Gannett, *Econ. Geol.*, **14**. 68, 1919; N. Branoic, *Giorn. Bibl. Tech. Internat.*, **1**. 3, 1925; F. L. Hess, *Tungsten Minerals and Deposits*, Washington, 1917; L. de Launay, *Compt. Rend.*, **138**. 712, 1904; *Min. World*, **30**. 387, 1910; W. H. Emmons, *Bull. U.S. Geol. Sur.*, 625, 1917;

J. J. Runner, *Pahasapa Quart.*, **5**. 13, 1916 ; W. Lindgren, *Econ. Geol.*, **2**. 453, 1906 ; T. L. Walker, *Min. World*, **31**. 547, 1909 ; W. S. Palmer, *Eng. Min. Journ.*, **105**. 780, 1918 ; S. H. Ball, *ib.*, **104**. 336, 1917 ; J. E. Spurr, *Trans. Amer. Inst. Min. Eng.*, **33**. 322, 1902 ; C. Bogenrieder, *Australian Min. Standard*, **40**. 557, 1908 ; G. B. Barham, *Min. Journ.*, **104**. 54, 1914 ; W. R. Jones, *ib.*, **120**. 135, 1918 ; *Trans. Inst. Min. Met.*, **29**. 320, 1920 ; J. C. Brown, *Min. Scient. Press.*, **115**. 302, 1917 ; N. B. Knox, *ib.*, **115**. 818, 1917 ; Anon., *ib.*, **115**. 298, 1917 ; S. J. Johnstone, *Journ. Soc. Chem. Ind.—Chem. Ind.*, **37**. 294 R, 334 R, 1918 ; C. Matignon, *Chim. Ind.*, **3**. 277, 422, 1920 ; F. L. Hess, *Eng. Min. Journ.*, **121**. 94, 1926 ; G. J. Young, *ib.*, **120**. 968, 1925 ; **121**. 605, 1926 ; W. R. Jones, *Trans. Inst. Min. Met.*, **29**. 320, 1920.

[4] P. Picot de la Peyrouse, *Journ. Mines*, **4**. 23, 1794 ; A. Damour, *Bull. Soc. Géol.*, (2), **5**. 108, 1848 ; E. Bertrand, *Bull. Soc. Min.*, **5**. 90, 1882 ; A. Lacroix, *ib.*, **31**. 349, 1908 ; *Minéralogie de la France et ses Colonies*, Paris, **4**. 287, 1910 ; J. Huré, *Bull. Soc. Ind. Min.*, (5), **9**. 99, 1916 ; A. Carnot, *Bull. Soc. Chim.*, (2), **20**. 488, 1873 ; *Compt. Rend.*, **79**. 477, 1873 ; *Ann. Chim. Phys.*, (5), **3**. 466, 1874 ; A. M. Finlayson, *Journ. Geol. Soc.*, **66**. 281, 1910 ; *Geol. Mag.*, (5), **3**. 19, 1910 ; A. Haenig, *Oesterr. Zeit. Berg. Hütt.*, **56**. 177, 1908 ; E. Terrell, *Mining Mag.*, **22**. 75, 1920 ; J. H. Collins, *Eng. Min. Journ.*, **81**. 1225, 1906.

[5] J. Huré, *Bull. Soc. Ind. Min.*, (5), **9**. 99, 1916.

[6] R. Douvillé, *Handbuch der regionalen Geologie*, Heidelberg, **3**. iii, 153, 1911 ; R. S. Lozano, *Bull. Soc. Ind. Min.*, (4), **15**. 268, 1911 ; W. T. Doerpinghaus, *Metall Erz*, **11**. 297, 1914 ; *Min. Journ.*, **119**. 717, 1917 ; H. A. McBride, *Mining World*, **32**. 993, 1909 ; J. Sacristan, *Rivista Minera*, **64**. 502, 1913 ; *Eng. Min. Journ.*, **97**. 27, 1914 ; *Min. Journ.*, **119**. 717, 1917 ; A. Carbonell and T. Figueroa, *Rivista Minera*, **68**. 28, 41, 1917 ; C. Granell, *Bol. Soc. Espan. Hist. Nat.*, **9**. 81, 1909 ; *Zeit. Kryst.*, **50**. 472, 1912 ; E. H. Pacheco, *Bol. Soc. Espan. Hist. Nat.*, **5**. 247, 1905 ; R. Ariza, *Rivista Minera*, **57**. 121, 1926 ; I. P. Pondall and J. Vazquez-Garriga, *Arq. Seminario Est. Galegos*, **3**. 1, 1929 ; I. Pargo and A. Arango, *Anal. Fis. Quim.*, **28**. 905, 1930.

[7] F. W. Foote and R. S. Ransom, *Eng. Min. Journ.*, **106**. 48, 1918 ; A. Pereira-Forjaz, *Compt. Rend.*, **173**. 1170, 1921 ; T. A. Down, *Min. Mag.*, **14**. 19, 1916 ; F. Bronckart, *Ann. Soc. Géol. Belg.*, **36**. 180, 1909 ; E. Ackermann, *Rev. Chim. Ind.*, **23**. 67, 1912 ; *Min. Eng. World*, **38**. 677, 1913 ; *Eng. Min. Journ.*, **104**. 1109, 1917 ; W. Preus, *ib.*, **83**. 843, 1907 ; C. von Bronhourst, *Chem. Ztg.*, **36**. 689, 1912 ; *Min. Scient. Press.*, **105**. 758, 1912 ; W. T. Dorpinghaus, *Metall Erz*, **2**. 297, 339, 1913 ; L. Duparc, *Tschermak's Mitt.*, (2), **38**. 100, 1925 ; W. Preus, *Eng. Min. Journ.*, **83**. 843, 1907 ; I. Parga and A. Arango, *Anal. Fis. Quim.*, **28**. 905, 1930 ; I. P. Pondal and J. V. Garriga, *ib.*, **28**. 79, 262, 1930.

[8] D. Lovisato, *Atti Accad. Lincei*, (5), **16**. i, 632, 1907 ; T. A. Down, *Mining Mag.*, **14**. 19, 1916 ; S. Traverso, *Resoceonti Riunioni, Soc. Min. Sarda*, **6**. 8, 1901 ; L. Columba, *Atti Accad. Lincei*, (5), **15**. i, 281, 1906 ; F. Zambonini, *ib.*, (5), **15**. i, 558, 1906 ; G. Carobbi, *ib.*, (5), **32**. ii, 79, 1923 ; *Gazz. Chim. Ital.*, **54**. 59, 1924 ; B. Granigg and J. H. Koritschoner, *Zeit. prakt. Geol.*, **21**. 484, 1913 ; G. Aichino, *Il Tungsteno*, Turin, 1916.

[9] C. Schmidt, *Zeit. Kryst.*, **24**. 137, 1895 ; **36**. 160, 1902.

[10] G. Weidinger, *Zeit. Pharm.*, **7**. 73, 1855 ; C. F. Rammelsberg, *Handbuch der Mineralchemie*, Leipzig, 309, 1860 ; J. Block, *Sitzber. Naturhist. Ver. Bonn.*, **2**. 68, 1905 ; G. A. Meerson, *Zhur. Erikladnoi Khim. Moscow*, **2**. 133, 1929 ; J. A. Krenner, *Tschermak's Mitt.*, (1), **5**. 9, 1875 ; L. Sipocz, *ib.*, (2), **7**. 270, 1886 ; F. Sandberger, *Sitzber. Akad. München*, 423, 1888 ; J. Helmhacker, *Eng. Min. Journ.*, **62**. 153, 1896.

[11] N. von Koulibin, *Proc. Russ. Min. Soc.*, (2), **3**. 1, 1868 ; L. von Mühlen, *Die Lagerstätten von Wolfram, Zinn, und Molybdän in Russland*, Stuttgart, 1926 ; M. Rusakoff, *Bull. Com. Geol. Leningrad*, **44**. 1, 1926 ; M. M. Tetiaeff, *Com. Géol. Gen. Appl. Petrograd*, 32, 1918 ; S. A. Doktorovich-Grebnitzky, *ib.*, 38, 1921 ; W. Beck and N. Teich, *ib.*, (2), **4**. 315, 1869 ; O. Trüstedt, *Bull. Com. Géol. Finlande*, 19, 1907 ; P. P. Sushchinsky, *Bull. Acad. St. Petersburg*, (6), **11**. 507, 567, 1917 ; S. J. Johnstone, *Journ. Soc. Chem. Ind.*, **37**. 334, 1918 ; K. K. Matfeeff, *Trans. Russ. Mining Congr.*, **7**. 201, 1928.

[12] W. Bruhns, *Die nutzbaren Mineralien und Gebirgsarten im deutschen Reiche*, Berlin, 566, 1906 ; R. Beck, *Zeit. prakt. Geol.*, **15**. 37, 1907 ; R. Schneider, *Pogg. Ann.*, **93**. 474, 1854 ; H. Suchanek, *Edel-Erden Erze*, **3**. 27, 1921 ; A. Jahn, *Mitt. Vogtl. Ges. Plauen*, 3, 1926.

[13] B. Doss, *Zeit. prakt. Geol.*, **23**. 138, 1915 ; G. Flink, *Bull. Geol. Inst. Upsala*, **5**. 96, 1901 ; P. P. Sushchinsky, *Bull. Acad. St. Petersburg*, (6), **11**. 507, 567, 1917.

[14] O. B. Böggild, *Medd. Grönland*, **32**. 179, 1905.

[15] L. L. Fermor, *Records Geol. Sur. India*, **36**. iv, 301, 1908 ; **63**. iii, 1, 1930 ; C. E. Low, *Board Trade Journ.*, **60**. 586, 1908 ; R. Bahadur, S. Sethu, and Rama Rau, *Mem. Geol. Sur. India*, **55**. i, 1, 1930.

[16] A. W. C. Bleeck, *Records Geol. Sur. India*, **43**. i, 48, 1913 ; E. Maxwell-Lefroy, *Eng. Min. Journ.*, **99**. 684, 1915 ; *Trans. Inst. Min. Met.*, **25**. 83, 1915 ; J. J. A. Page, *ib.*, **25**. 109, 1915 ; W. R. Jones, *Min. Mag.*, **17**. 230, 1917 ; J. Coggin-Brown, *Journ. Soc. Chem. Ind.*, **39**. 44, T, 1920 ; *The Geology of the Tavoy District*, Tavoy, 1917 ; J. Coggin-Brown and A. M. Heron, *Records Geol. Sur. India*, **50**. ii, 101, 1919 ; E. M. Lefroy, *Eng. Min. Journ.*, **99**. 684, 1915 ; *Trans. Inst. Min. Met.*, **25**. 83, 1915 ; H. D. Griffiths, *ib.*, **27**. 60, 1917 ; C. W. Charter, *Iron Coal Trades Rev.*, **90**. 880, 1915 ; *Trans. Inst. Min. Eng.*, **49**. 628, 1915 ; H. B. Osborn, *Eng. Min. Journ.*, **96**. 636, 778, 1913 ; H. Adamson, *Bull. Imp. Inst.*, **16**. 76, 1918 ; J. M. Campbell, *Econ. Geol.* **15**. 511, 1920 ; *Mining Mag.*, **20**. 76, 1919 ; G. D. Ricketts, *Mining Journ.*, **76**. 479, 1904.

[17] W. R. Jones, *Journ. Geol. Soc.*, **72**. 165, 1916 ; J. B. Scrivenor, *Min. Journ.*, **114**. 384, 406, 433, 1916 ; *Min. Mag.*, **14**. 347, 1916 ; Anon., *ib.*, **14**. 347, 1916 ; **17**. 179, 211, 1917 ; **19**. 181, 1918 ; H. Brelich, *ib.*, **13**. 263, 1915.

[18] *Commerce Rep. U.S.A.*, 142, 1918.

[19] T. Wada, *Minerals of Japan*, London, **77**. 1904 ; Anon., *Bull. Geol. Sur. Japan*, **17**. 23, 1904 ; K. Jimbo, *Journ. Tokyo Coll. Science*, **11**. 213, 1899 ; S. Kozu and W. Watanabe, *Proc. Pan-Pacific Science Congr.*, **3**. i, 839, 1926.

[20] R. Slessor, *Eng. Min. Journ.*, **109**. 344, 1920 ; Anon., *Chem. News*, **121**. 6, 1920 ; *Journ. Soc. Arts*, **68**. 509, 1920 ; *Min. Scient. Press.*, **116**. 84, 1918 ; *Eng. Min. Journ.*, **105**. 24, 1918 ; P. Jereméeff, *Proc. Russ. Min. Soc.*, **31**. 404, 1894 ; T. Pakliang, *Recherches sur quelques minérais chinois de tungstène et de molybdène*, Paris, 1928.

[21] Anon., *Iron Coal Trades Rev.*, **93**. 42, 1916.

[22] Anon., *Bull. Impt. Inst.*, **13**. 252, 1915 ; H. B. Maufe, B. Lightfoot and A. E. V. Zealley, *Southern Rhodesia Geol. Sur.*, 3, 1918 ; H. B. Maufe, *ib.*, 1, 1917 ; 4, 1918 ; *Tungsten Ores in Southern Rhodesia*, Salisbury, 1918 ; A. E. V. Zealley, *The Tungsten Deposits of Essexvale, Umzingwane District*, Bulawayo, 1917 ; *Min. Mag.*, **17**. 92, 1917 ; Anon., *Chem. News*, **116**. 291, 1917 ; Anon., *Journ. Roy. Soc. Arts*, **65**. 696, 1917 ; P. A. Wagner, *South African Min. Journ.*, **24**. 344, 1915 ; **25**. 311, 1916 ; J. P. Johnson, *The Ore Deposits of South Africa*, London, 40, 1908 ; Anon., *Chem. News*, **116**. 291, 1917 ; W. R. Rumbold, *Trans. Amer. Inst. Min. Eng.*, **39**. 783, 1909 ; S. J. Johnstone, *Journ. Soc. Chem. Ind.*, **37**. 334, 1918.

[23] T. L. Walker, *Report on the Tungsten Ores of Canada*, Ottawa, 1909 ; and 1914 ; *Canadian Min. Journ.*, **29**. 302, 1908 ; *Journ. Canadian Min. Inst.*, **11**. 367, 1908 ; *Econ. Geol.*, **6**. 396, 1911 ; *Min. World*, **30**. 747, 1909 ; *Summary Rep. Canadian Geol. Sur.*, 228, 1909 ; 247, 1916 ; R. A. A. Johnson, *Rept. Canada Geol. Sur.*, **11**. 10, 1898 ; *Min. Resources Canada Geol. Sur.*, 1, 1904 ; J. S. de Lury, *Canadian Min. Journ.*, **39**. 186, 1918 ; A. C. Ross, *Eng. Min. Journ.*, **68**. 370, 1899 ; A. J. R. Atken, *Geol. Mag.*, (5), **2**. 116, 1905 ; H. Piers, *Trans. Nova Scotia Inst. Science*, **16**. 38, 1928 ; A. L. McCallum, *ib.*, **12**. iii, 350, 1912 ; *Canadian Min. Journ.*, **29**. 456, 1908 ; Anon., **31**. 549, 1910 ; *Eng. Min. Journ.*, **88**. 729, 1910 ; A. A. Hayward, *Journ. Min. Soc. Nova Scotia*, **15**. 65, 1909 ; E. R. Faribault, *ib.*, **15**. 159, 1919 ; *Min. World*, **33**. 659, 1910 ; *Canadian Min. Journ.*, **31**. 428, 1910 ; *Summary Rep. Canadian Geol. Sur.*, 150, 1909 ; G. A. Young, *ib.*, I, 1909 ; V. G. Hills, *Min. Scient. Press.*, **106**. 448, 1913 ; W. L. Swanson, *Univ. Toronto Geol. Stud.*, 20, 1925 ; G. B. Barham, *Mining Journ.*, **104**. 54, 1914 ; S. J. Johnstone, *Journ. Soc. Chem. Ind.*, **37**. 334, 1918.

[24] A. Knopf, *Science*, (2), **27**. 924, 1908 ; *Bull. U.S. Geol. Sur.*, 345, 358, 1908 ; B. L. Johnson, *ib.*, 442, 1910 ; A. H. Brooks, *ib.*, 480, 1911 ; F. H. Moffit, *ib.*, 533, 1913 ; A. M. Bateman, *Econ. Geol.*, **13**. 112, 1918.

[25] W. P. Blake, *Minerals of Arizona*, Tuscon, 1909 ; *Eng. Min. Journ.*, **65**. 608, 1898 ; *Min. Ind.*, **7**. 720, 1898 ; *Trans. Amer. Inst. Min. Eng.*, **28**. 543, 1898 ; J. A. Church, *ib.*, **33**. 3, 1903 ; Anon., *Eng. Min. Journ.*, **90**. 1103, 1911 ; W. P. de Wolf, *ib.*, **101**. 680, 1916 ; F. Rickard, *ib.*, **77**. 263, 1904 ; L. O. Kellogg, *Econ. Geol.*, **1**. 654, 1906 ; A. C. Rubel, *Bull. Bur. Mines Arizona Univ.*, 11, 1916 ; F. N. Guild, *The Mineralogy of Arizona*, Easton, Pa., 1910 ; R. W. Richards, *Min. Science*, **57**. 93, 1908 ; F. C. Schrader, *Bull. U.S. Geol. Sur.*, 340, 1907 ; J. M. Hill, *ib.*, 340. 1907 ; 430, 1910 ; F. C. Schrader and J. M. Hill, *ib.*, 582, 1915 ; F. L. Hess, *ib.*, 380, 1908 ; W. A. Scott, *Eng. Min. World*, **45**. 143, 1916 ; A. Wolf, *Eng. Min. Journ.*, **101**. 680, 1916.

[26] H. G. Hanks, *Rep. California State Mineralogist*, 1, 1884 ; J. H. Williams, *Min. Scient. Press.*, **103**. 545, 1911 ; W. H. Storms, *ib.*, **113**. 768, 1916 ; C. T. Hutchinson, *ib.*, **112**. 797, 1916 ; Anon., *ib.*, **115**. 95, 1917 ; F. L. Hess, *Bull. U.S. Geol. Sur.*, 340, 1907 ; A. Knopf, *ib.*, 640, 1917 ; S. H. Dolbear, *Eng. Min. Journ.*, **90**. 904, 1910 ; L. L. Wittich, *ib.*, **102**. 295, 1916 ; R. S. Baverstock, *Mining World*, **24**. 414, 1906.

[27] T. B. Comstock, *Eng. Min. Journ.*, **38**. 29, 45, 98, 200, 315, 328, 1885 ; C. A. Cooper, *ib.*, **67**. 499, 1899 ; H. J. Wolf and P. P. Barbour, *ib.*, **102**. 165, 1916 ; W. E. Greenawalt, *Cornell Cir. Eng.*, **20**. 197, 1912 ; *Eng. Min. Journ.*, **83**. 951, 1907 ; W. C. Prosser, *ib.*, **90**. 320, 1910 ; R. D. George, *ib.*, **95**. 186, 1913 ; L. A. Palmer, *ib.*, **96**. 99, 1913 ; H. J. Wolf and P. P. Barbour, *ib.*, **102**. 165, 186, 1916 ; H. A. Lee, *ib.*, **71**. 466, 1900 ; *Bull. Min. Bur. Colorado*, **4**. 12, 1901 ; **5**. 20, 1902 ; J. B. Ekeley, *Univ. Colorado Studies*, **6**. 93, 1909 ; *Min. World*, **30**. 280, 1909 ; F. L. Ransome, *Bull. U.S. Geol. Sur.*, 182, 1901 ; E. S. Bastin, *ib.*, 620, 1910 ; W. Lindgren, *Econ. Geol.*, **2**. 453, 1907 ; **9**. 262, 1915 ; W. Lindgren and F. L. Ransome, *Prof. Paper U.S. Geol. Sur.*, **54**. 127, 1906 ; Anon., *Min. Reporter*, **51**. 5, 133, 1905 ; L. A. Palmer, *Min. Eng. Rev.*, **5**. 480, 1913 ; *Eng. Min. Journ.*, **96**. 99, 1913 ; A. J. Moses, *Amer. Journ. Science*, (4), **20**. 281, 1905 ; R. D. George and R. D. Crawford, *Colorado Geol. Sur.*, **6**. 93, 1908 ; R. D. George, *Mining World*, **85**. 277, 1909 ; *Proc. Colorado Scient. Soc.*, **9**. 181, 1909 ; V. G. Hills, *ib.*, **9**. 135, 1909 ; H. R. van Wagenen, *Bull. Colorado School Mines*, **3**. 138, 1909 ; *Mining Mag.*, **13**. 327, 1906 ; R. C. McKenna, *ib.*, **57**. 1281, 1916 ; J. R. Wood, *Min. Science*, **62**. 11, 1910 ; P. H. Carl, *ib.*, **63**. 92, 1911 ; T. J. Dalzell, *ib.*, **63**. 498, 1911 ; *Rept. Colorado Bur. Mines*, 21, 1911 ; M. B. Tomblin, *Bull. Boulder County Metal Mining Assoc.*, 3, 1912 ; E. Ackermann, *Rev. Chim. Ind.*, **22**. 114, 1911 ; C. T. Kirk, *Min. Scient. Press.*, **112**. 791, 1916 ; F. L. Hess and W. T. Schaller, *Bull. U.S. Geol. Sur.*, 583, 1914 ; F. L. Hess, *ib.*, 652, 1917 ; J. M. Hill, *ib.*, 620, 1916 ; R. S. Fitch and G. F. Laughlin, *Econ. Geol.*, **11**. 30, 1916 ; T. Tonge, *Mining Journ.*, **78**. 92, 1905 ; A. B. Frenzel, *Mining World*, **23**. 385, 1905.

[28] A. Gurlt, *Trans. Amer. Inst. Min. Eng.*, **22**. 236, 1893; W. H. Hobbs, *Bull. U.S. Geol. Sur.*, 213, 1903; *Ann. Rept. U.S. Geol. Sur.*, **22**. ii, 7, 1901.

[29] H. S. Auerbach, *Eng. Min. Journ.*, **86**. 1146, 1908; G. P. Rowe, *Min. World*, **29**. 739, 777, 843, 1908; **30**. 11, 89, 117, 318, 357, 428, 1909; F. L. Hess, *Bull. U.S. Geol. Sur.*, 652, 1917; J. B. Umpleby, *ib.*, 528, 1913; F. L. Ransome and F. C. Calkins, *Prof. Paper U.S. Geol. Sur.*, **62**. 103, 1908.

[30] E. Haworth, *Amer. Geol.*, **1**. 294, 1888; H. A. Wheeler, *Eng. Min. Journ.*, **103**. 21, 1917.

[31] R. Pearce, *Trans. Amer. Inst. Min. Eng.*, **16**. 64, 1888; C. W. Goodale and W. A. Ackers, *ib.*, **18**. 248, 1890; F. Tomek, *Min. World*, **28**. 63, 1908; W. H. Weed, *Prof. Paper U.S. Geol. Sur.*, **74**. 80, 1912; C. E. Morris, *Eng. Min. Journ.*, **92**. 784, 1912; A. N. Winchell, *Bull. U.S. Geol. Sur.*, 574, 1914.

[32] F. B. Weeks, *Ann. Rept. U.S. Geol. Sur.*, **21**. vi, 319, 1901; *Bull. U.S. Geol. Sur.*, 213, 1903; 340, 1907; *Eng. Min. Journ.*, **72**. 8, 1902; F. B. Smith, *ib.*, **73**. 304, 1902; J. A. Burgess, *Econ. Geol.*, **6**. 22, 1911; A. S. Eakle, *Bull. California Dept. Geol.*, **7**. 1, 1912; F. L. Hess and W. F. Hunt, *Amer. Journ. Science*, (4), **36**. 51, 1913; P. B. McDonald, *Min. Scient. Press.*, **112**. 40, 1916; F. L. Hess, *Bull. U.S. Geol. Sur.*, 652, 1917.

[33] W. Lindgren, L. C. Graton and C. H. Gordon, *Prof. Paper U.S. Geol. Sur.*, **68**. 180, 292, 336, 1910; F. L. Hess, *Bull. U.S. Geol. Sur.*, 652, 1917; H. H. Taft, *Eng. Min. World*, 44, 1047, 1916.

[34] A. J. R. Atkin, *Geol. Mag.*, (5), **2**. 116, 1905.

[35] W. Lindgren, *Ann. Rept. U.S. Geol. Sur.*, **22**. ii, 644, 1901.

[36] G. H. Williams, *Amer. Journ. Science*, (3), **44**. 50, 1893.

[37] J. D. Irving, *Prof. Paper U.S. Geol. Sur.*, **26**. 43, 1904; *Min. Rept.*, **10**. 430, 1904; *Bull. U.S. Geol. Sur.*, 225, 1904; *Trans. Amer. Inst. Min. Eng.*, **31**. 683, 1901; R. W. Raymond, *ib.*, **31**. 1025, 1901; C. C. O'Harra, *Bull. South Dakota School Mines*, **6**. 11, 1902; V. Ziegler, *ib.*, **10**. 218, 1914; *Min. Scient. Press.*, **108**. 604, 654, 1914; E. H. Quinney, *ib.*, **65**. 45, 1913; J. Simmons, *Min. Eng. World*, **43**. 816, 1915; *Min. Rep.*, **6**. 11, 1902; Anon., *ib.*, **10**. 217, 1904; F. L. Hess, *Bull. U.S. Geol. Sur.*, 380, 1908; 652, 1917.

[38] T. B. Comstock, *Rept. Geol. Sur. Texas*, 597, 1890; F. W. Simonds, *Bull. Texas Univ. Min. Sur.*, **5**. 3, 1902; *Science*, (2), **14**. 796, 1902; F. L. Hess, *Bull. U.S. Geol. Sur.*, 340, 1908.

[39] F. L. Hess, *Bull. U.S. Geol. Sur.*, 652, 1917.

[40] W. S. Thyng, *Eng. Min. Journ.*, **73**. 418, 1902; M. H. Joseph, *ib.*, **81**. 409, 1906; H. Bancroft, *Bull. U.S. Geol. Sur.*, 430, 1910; 550, 1914; A. Wolf, *Mines Minerals*, **31**. 307, 1910; Anon., *Erzbergbau*, 343, 1910; W. T. Schaller, *Journ. Washington Acad.*, **1**. 24, 1911; L. K. Armstrong, *Min. Scient. Press.*, **102**. 753, 1911.

[41] W. R. Ingalls, *Trans. Amer. Inst. Min. Eng.*, **27**. 428, 1897; J. G. Aguilera, *ib.*, **32**. 506, 1902.

[42] A. von Keyserling, *Zeit. prakt. Geol.*, **17**. 156, 1909; *Min. Mag.*, **18**. 230, 1918; G. Bodenbinder, *Zeit. prakt. Geol.*, **12**. 409, 1904; R. Beder, *Min. Scient. Press.*, **116**. 204, 1918; *Bol. Argentina Agric.*, 12, 1916; 5, 1922; *Bull. Suisse Min. Petr.*, **1**. 44, 1921; E. Kittl, *Rev. Min. Soc. Argentina*, **2**. 17, 33, 148, 1930.

[43] H. C. Tarnawiecki, *Min. Journ.*, **94**. 687, 1911; E. Weckwarth, *ib.*, **85**. 24, 1909; C. G. Fink, *Min. Ind.*, **23**. 753, 1914; E. A. V. de Habich, *El Yacimiento de Tungsteno de Lircay*, Lima, 1904; *Bol. Cuerpo Ing. Min. Peru*, 11, 1904; Y. Leon, *ib.*, 90, 1918; Anon., *Min. Eng. World*, **42**. 302, 1915.

[44] A. C. Kerr, *Board Trade Journ.*, **71**. 40, 1909; Anon., *Chem. Ind.*, **33**. 792, 1911; I. D. Ossa, *Bol. Soc. Nac. Min. Santiago*, (3), **28**. 202, 1916; *Min. Journ.*, **115**. 832, 1916; B. L. Miller and J. T. Singewald, *The Mineral Deposits of South America*, New York, 1919; I. Domeyko, *Ann. Mines*, (6), **16**. 537, 1869.

[45] B. L. Miller and J. T. Singewald, *The Mineral Deposits of South America*, New York, 1919; *Eng. Min. Journ.*, **102**. 1006, 1916; G. W. Schneider and B. L. Miller, *ib.*, **109**. 787, 1920; G. W. Wepfer, *ib.*, **97**. 1251, 1914; Anon., *ib.*, **96**. 636, 1913; **102**. 464, 1916; P. F. Bliek and M. G. F. Soehnlein, *ib.*, **101**. 173, 1916; G. Blanco, *Board Trade Journ.*, **74**. 23, 1910; L. J. Spencer, *Min. Mag.*, **14**. 334, 1905; G. F. J. Preumont, *Trans. Inst. Min. Met.*, **28**. 122, 1919.

[46] Anon., *Min. Scient. Press.*, **115**. 692, 1917; F. Freise, *Zeit. prakt. Geol.*, **18**. 143, 1909.

[47] A. Liversidge, *The Minerals of New South Wales*, London, 85, 1888; J. E. Carne, *Notes on the Occurrence of Tungsten Ores in N.S.W.*, Sydney, 1898; *Min. Resources N.S.W. Geol. Sur.*, 2, 1898; 15, 1911; *Bull. Imp. Inst.*, **10**. 688, 1912; E. C. Andrews, *ib.*, **8**. 138, 1905; E. F. Pitman, *Bull. N.S.W. Geol. Sur.*, **4**. 294, 1901; W. E. Cameron, *Wolfram and Molybdenite Mining in Queensland*, Brisbane, 1904; *Rept. Queensland Geol. Sur.*, 188, 1904; 248, 251, 1915; *Queensland Govt. Min. Journ.*, **4**. 10, 1903; F. J. Cherry, *ib.*, **9**. 263, 1908; Anon., *ib.*, **9**. 226, 1908; A. R. McDonald, *ib.*, **12**. 110, 1911; L. C. Ball, *ib.*, **12**. 559, 1911; **14**. 7, 70, 1913; **15**. 568, 617, 1914; E. C. Saint-Smith, *ib.*, **17**. 57, 1916; B. Dunstan, *Queensland Govt. Min. Journ.*, **6**. 334, 1905; *Ann. Rep. Queensland Mines*, 151, 1904; H. Conder, *Eng. Min. Journ.*, **78**. 170, 1905; Anon., *ib.*, **78**. 900, 1905; E. S. Simpson and C. G. Gibson, *Bull. West Australia Geol. Sur.*, 30, 1907; W. H. Twelvetrees, *Rep. Tasmania Geol. Sur.*, 1, 1907; 14, 1913; L. Hills and L. L. Waterhouse, *ib.*, 1, 1916; C. Anderson, *Rec. Australian Museum*, **6**. 414, 1907; E. C. Playford, *Rept. Northern Territory*, 28, 1908; Anon., *Iron Coal Trades Rev.*, **88**. 914, 1914; C. J. Gray and R. J. Winters, *Bull. Northern Territory, Australia*, 15, 1916; T. G. Oliver, *ib.*, 21, 1916;

C. W. Gudgeon, *Proc. Australian Inst. Min. Eng.*, **21**. 37, 1916 ; *Australian Min. Standard*, **50**. 409, 1913 ; *Min. Mag.*, **15**. 103, 1916 ; Anon., **19**. 258, 1918 ; T. W. E. David, *Journ. Roy Soc. N.S.W.*, **45**. 1, 1911 ; Anon., *Min. Journ.*, **119**. 745, 1917 ; *Journ. Ind. Eng. Chem.*, **9**. 99, 1917 ; A. E. Kitson, *The Economic Minerals and Rocks of Victoria*, Melbourne, 1906 ; W. D. Campbell, *Ann. Rep. Geol. Sur. West Australia*, 1, 1908 ; S. J. Johnstone, *Journ. Soc. Chem. Ind.*, **37**. 334, 1918 ; F. F. Clotten, *Tschermak's Mitt.*, (2), **24**. 137, 1906 ; J. Plummer, *Mining Journ.*, **76**. 404, 1904.

[48] A. M. Finlayson, *Trans. N.Z. Inst.*, **40**. 110, 1907 ; C. W. Gudgeon, *Australian Min. Standard*, 48, 1913 ; *Proc. Austral. Inst. Min. Eng.*, **21**. 37, 1916 ; *Min. Mag.*, **15**. 103, 1916 ; A. McKay, *Rept. N.Z. Geol. Expl.*, 84, 1890.

[49] R. H. Rastall and W. H. Wilcockson, *Tungsten Ores*, London, 1920 ; W. Borchers, *Min. Ind.*, **8**. 632, 1899 ; A. S. Brown, *ib.*, **13**. 409, 1904 ; R. Meeks, *ib.*, **14**. 557, 1905 ; **15**. 744, 1906 ; W. L. Fleming, *ib.*, **18**. 687, 1909 ; C. G. Fink, *ib.*, **22**. 762, 1913 ; **23**. 745, 1914 ; **24**. 685, 1915 ; Anon., *ib.*, **2**. 615, 1893 ; **3**. 484, 1894 ; **5**. 471, 1896 ; **6**. 651, 1897 ; **7**. 719, 1898 ; **9**. 657, 1900 ; **10**. 647, 1901 ; **11**. 598, 1902 ; **16**. 888, 1907 ; **17**. 827, 1908 ; **19**. 662, 1910 ; **20**. 724, 1911 ; **21**. 842, 1912 ; *Engg.*, **99**. 442, 1915 ; **104**. 128, 1917 ; *Eng. Min. Journ.*, **93**. 39, 1912 ; **100**. 50, 1915 ; **103**. 1, 1917 ; **104**. 891, 1917 ; *Min. Scient. Press.*, **115**. 473, 711, 1917 ; **116**. 26, 1917 ; *Chem. Trade Journ.*, **59**. 528, 1916 ; *Elect. World*, **50**. 757, 1907 ; K. Thomas, *Min. World*, **28**. 164, 1908 ; D. T. Day, *Min. Res. U.S. Geol. Sur.*, 574, 1884 ; 218, 1886 ; J. H. Pratt, *ib.*, 257, 1900 ; 261, 1901 ; 285, 1902 ; 304, 1903 ; 326, 1904 ; 410, 1905 ; F. L. Hess, 522, 1906 ; 711, 1907 ; 726, 1908 ; 577, 1909 ; 725, 1910 ; 941, 1911 ; 987, 1912 ; 937, 1914 ; 805, 1915 ; G. O. Smith, *Min. Eng. World*, **43**. 58, 1915 ; R. C. McKenna, *Iron Trade Rev.*, **57**. 1281, 1915 ; E. M. Lefroy, *Eng.*, **120**. 320, 1915 ; C. F. Willis, *Min. Scient. Press.*, **112**. 824, 1916 ; H. C. Morris, *ib.*, **104**. 885, 1912 ; C. Hardy, *ib.*, **115**. 711, 1917 ; *Eng. Min. Journ.*, **105**. 91, 1917 ; F. W. Foote, *ib.*, **105**. 90, 1917 ; W. M. Foote, *Eng. Min. World*, **44**. 279, 1916 ; C. C. O'Harra, *Pahasapa Quart.*, **5**. 2, 1916 ; L. Moser, *Oesterr. Chem. Ztg.*, **26**. 67, 1923 ; H. R. van Wegenen, *Chem. Eng.*, **4**. 217, 284, 1906 ; H. Carlborg, *Jernkontorets Ann.*, (2), **114**. 455, 1930 ; C. C. Fink, *Min. Ind.*, **38**. 637, 1929 ; R. Webers, *Metallbörse*, **20**. 425, 481, 594, 708, 764, 930, 987, 1930.

[50] F. L. Hess, *Bull. U.S. Geol. Sur.*, 652, 1917.

[51] H. St. C. Deville, *Ann. Chim. Phys.*, (5), **61**. 344, 1861 ; M. Mazade, *Compt. Rend.*, **32**. 685, 1851 ; F. Zambonini, *Amer. Min.*, **12**. 1, 1927.

§ 3. The Extraction of Tungsten Trioxide

The products usually obtained from tungsten ores are (i) compounds, like tungsten trioxide or tungstates, employed in the arts as pigments, mordants, etc. ; (ii) crude tungsten, usually pulverulent, employed for making ferrotungsten, and other alloys ; and (iii) purified metal in the form of sheet, rod, or wire, for use in lamps, X-ray tubes, thermionic valves, etc. The mining of tungsten ores does not present any peculiarities different from those used in mining other ores of a similar nature. The ore as mined is commonly associated with tinstone. The milling and concentration [1] of wolfram ore may involve the use of a magnetic separator since wolfram is fairly magnetic in virtue of the contained iron, while tinstone is virtually non-magnetic. A separation with less than one per cent. of tin oxide with the wolframite is rarely possible. Scheelite is not usually magnetic, but it is not commonly found associated with tinstone. When tinstone is present, a chemical process is required for the separation. The average amount of tungsten trioxide in the concentrate is about 65 per cent.

Scheelite is easily decomposed by heating it with conc. hydrochloric or nitric acid whereby calcium chloride or nitrate is formed, and hydrated tungsten trioxide. The latter can be purified by dissolving the hydrate in a soln. of ammonium carbonate and ammonia, as indicated below. This process was used by A. E. Nordenskjöld.[2] According to G. Gin, scheelite may be fused in a reverberatory furnace with potassium fluoride so as to form soluble potassium tungstate and insoluble calcium fluoride. The soln. of the tungstate is then decomposed by acid in the usual manner. P. Schwarzkopf heated the ore in air to form tungsten trioxide, and when oxidation was complete, he sublimed the trioxide in a current of air.

The extraction of tungsten trioxide by treating wolframite with acids.[3]—The finely-powdered mineral is digested with conc. hydrochloric acid, renewing the acid from time to time, and adding a little nitric acid towards the end of the operation, so as to oxidize and dissolve the iron as a ferric salt. The operation is continued until the ferric and manganic oxides have passed into soln., and the brown residue is changed to a yellow colour. The undissolved residue consists of hydrated tungsten trioxide, undissolved wolframite, and silica; it is then well-washed, and shaken up with aq. ammonia. The hydrated tungsten trioxide passes into soln.; and on evaporating the filtered soln., crystals of ammonium tungstate are formed. The ammonium salt is then ignited in air to form tungsten trioxide. Modifications of the process were described by J. B. von Borck, J. B. A. Dumas, B. Franz, W. Lotz, J. C. G. de Marignac, J. Persoz, J. Philipp, A. Riche, E. R. Schneider, and E. Zettnow. The product is of inferior purity. If desired, the small proportion of columbium and tantalum can be removed by treating the product with ammonium sulphide which dissolves only the tungsten trioxide. The soln. is acidified with hydrochloric acid to precipitate hydrated tungsten trioxide. This is washed, dried, and ignited. In another process, the finely-divided ore is digested with 50 per cent. sulphuric acid, heated by superheated steam in lead pipes immersed in the liquid. In 3 hrs. the liquid containing iron and manganese is decanted off, and the extraction repeated 2 or 3 times with 30 per cent. sulphuric acid. The residue is mixed with 20 per cent. sodium chloride and half this weight of sodium nitrate, and enough sulphuric acid added to evolve hydrogen chloride and nitrous fumes. This is repeated 2 or 3 times to oxidize the remaining iron and manganese. The hydrated tungsten trioxide mixed with any insoluble matter, like silica, remains as a sludge. It is washed and dried. The iron and manganese sulphates are recovered by evaporating the acid liquors. L. Weiss discussed the opening of wolframite by treatment with conc. hydrochloric, hydrofluoric, sulphuric or nitric acid, or with aqua regia. K. Anjow used dil. sulphuric acid at 180° under press. for opening up the finely-divided ore.

The extraction of tungsten trioxide by heating wolframite with fluxes.—J. B. Richter,[4] and J. B. von Borck fused the wolframite with four times its weight of potassium nitrate—or a mixture of sodium carbonate and potassium nitrate, or a mixture of sodium and potassium carbonates—extracted the cold product with water; precipitated calcium tungstate from the filtrate by the addition of calcium chloride; decomposed the washed calcium salt with nitric acid; and washed the hydrated tungsten trioxide with water. E. F. Anthon boiled the soln. of potassium tungstate for a quarter of an hour with an excess of hydrochloric acid, dissolved the washed hydrated tungsten trioxide in aq. ammonia; and evaporated the soln. for ammonium tungstate. C. F. Bucholz, and J. J. Berzelius fused the wolframite with twice its weight of potassium carbonate; B. Franz, and J. Philipp used 150 parts of ore, 100 parts of sodium carbonate, and 15 parts of potassium nitrate; L. Mayer, and G. C. Wittstein used one part of wolframite, one of potassium nitrate, and 2 parts of potassium carbonate; C. Scheibler, and E. Zettnow used 33 to 50 per cent. of sodium carbonate; W. B. Stoddard and I. Hochstadter used a mixture of ore, charcoal, and sodium nitrate; R. W. Stimson, alkali nitrate; and A. Riche used 17 parts of sodium carbonate with 10 parts of wolframite. The processes in use are more or less modified forms of R. Oxland's process in which the ore is first fused with sodium carbonate, and the sodium tungstate extracted by leaching with water. Modifications were described by F. A. Bernoulli, K. Christl, G. Bessa, A. K. Huntington, R. Derenbach, etc.

C. H. Jones, describing the process in use in North Chicago, said that the hand-picked ore is crushed and ground to a coarse powder; and mixed with soda-ash in a ball-mill so as to pass 100's lawn—one part each of tungsten trioxide and sodium carbonate plus a 15 per cent. excess of the latter. About 150 kgrms. of the mixture are charged into a reverberatory furnace and raked by hand for a couple of hours while the temp. is kept at about 800°. This allows a free access of air to oxidize the iron and manganese respectively to Fe_2O_3 and Mn_3O_4. The product is removed from the furnace, cooled, and crushed; and the sodium tungstate extracted by leaching with water. The clear liquor is heated by a jet of live steam, and a soln. of calcium chloride is added to precipitate calcium tungstate. This is washed by decantation, and then treated with hydrochloric acid. The yellow precipitate is washed by means of a suction pump; and dried. Its composition approximates: H_2WO_4, 99·53; FeO, 0·02; Al_2O_3, 0·05; CaO, 0·20; and SiO_2, 0·20 per cent. J. B. Ekeley and W. B. Stoddard added sodium chloride to the fusion mixture to hasten the reaction. It is then necessary to add a little sodium nitrate or chlorate as oxidizing agent. The General Electric Co., and N. T. Gordon and A. F. Spring used a continuous process.

F. Wöhler melted one part of wolframite with 2 parts of calcium chloride for an hour, and extracted the cold, powdered mass with boiling water; the chlorides of calcium, manganese, and iron passed into soln. The residual calcium tungstate was treated with conc. hydrochloric acid; the washed residue was dissolved in aq. ammonia, and the soln. evaporated for ammonium tungstate; the product was heated to redness for tungsten trioxide. F. Jean mixed powdered wolframite with 3 per cent. of calcium carbonate and 20 to 30 per cent. of sodium chloride, and heated the mixture for half an hour to dull redness. When the mixture is cold, it is pulverized, and then boiled for a quarter of an hour with hydrochloric acid, which dissolves the lime, and the oxides of iron and manganese, with the disengagement of chlorine, leaving the whole of the tungstic acid in the insoluble state as a lemon-yellow crystalline powder, which is purified by washing with acid. With calcium carbonate, without sodium chloride, it was found impossible to decompose the wolframite completely; but with about 20 per cent. of pure lime, the decomposition was easily effected at a dull red-heat. Sulphates, alkaline carbonates, or calcium chloride may replace the sodium chloride. L. Weiss compared the result obtained by opening up the wolframite by heating it with ammonium fluoride; sodium hydroxide; calcium carbonate—alone or mixed with calcium or sodium chloride; with calcium chloride; or with magnesium compounds. He recommended fusing a mixture of 4 parts of wolframite with one part of each of calcium carbonate and chloride, and decomposing the product with an acid. If magnesium carbonate be employed, the product contains red crystals of magnesium tungstate which are not decomposed by acids. G. Gin heated a mixture of wolframite and magnesium chloride on the hearth of a reverberatory furnace and found that the manganese and iron are volatilized as chlorides. The aq. extract of the cold mass furnishes a soln. from which, on evaporation, crystals of magnesium tungstate can be obtained. This salt is decomposed by hot, conc. hydrochloric acid leaving insoluble hydrated tungsten trioxide.

When tin is present in appreciable quantities, G. Gin recommended fusing the ore mixed with potassium hydrosulphate in a furnace with the hearth made of silica agglomerated with pitch. The mixture is stirred and run from the furnace. The cold, powdered mass is digested with water—soluble sulphates pass into soln., and an insoluble acid potassium tungstate remains along with silica, stannic oxide, and insoluble sulphates. The dried mass is treated with a warm soln. of ammonium carbonate when the potassium tungstate passes into soln., whilst the stannic oxide, sulphates, and silica remain. The evaporation of the soln. furnishes ammonium tungstate which is converted into tungsten trioxide by ignition. The ammoniacal soln. can be treated with hydrogen sulphide, and ammonium sulphotungstate is deposited in orange-red crystals which, on ignition and roasting, pass into tungsten trisulphide and then to the trioxide. The Elektrochemische Fabrik used sodium hydrosulphate with an excess of sulphuric acid in place of potassium hydrosulphate. The aq. extract contains soluble metal sulphates and sodium tungstate. The metals can be precipitated by electrolysis; and the sodium sulphate crystallized out. Hydrochloric acid then precipitates hydrated tungsten trioxide. H. Brandenburg and A. Weyland, and F. E. Clotten employed a modification of the hydrosulphate fusion process.

The extraction of tungsten trioxide from wolframite by alkali-lye.—Tungsten trioxide can be extracted from wolframite by treatment with conc. soda-lye or potash-lye. The tungsten can be recovered from the liquor by crystallization, by precipitation with acid, or precipitation as calcium tungstate, etc. E. K. Jenckes recommended the process. G. A. Hempel carried out the extraction in an autoclave under press. by mixture of alkali-lye with enough lime to ensure the precipitation of silica and tin, but not enough to precipitate calcium tungstate. The tungsten trioxide is recovered in the usual way. W. B. Gero and C. V. Iredell digested in boiling soda-lye ground wolframite concentrates and added calcium chloride to the resulting soln., whilst the resulting calcium tungstate was digested with boiling hydrochloric acid, and the tungstic acid converted into ammonium paratungstate. The latter was ignited for tungstic oxide. L. Weiss discussed the results obtained by extraction with alkali-lye.

The extraction of tungsten trioxide from wolframite by volatilization as chloride.—The processes based on the volatility of the chloride are not practicable with low-grade ores unless other metals—*e.g.* tin—can be recovered at the same time. In W. H. Dyson and L. Aitchison's process, the wolframite is heated to 600° in a current of equal vols. of chlorine and hydrogen chloride to remove the tin ; and the temp. is then raised to 900° to distil off the iron, manganese, and tungsten chlorides. The distillate is collected in water so as to precipitate the hydrated tungsten trioxide. O. J. Stannard mixed the crushed ore with carbonaceous material, and heated the mixture to redness. The product is then heated at about 300° in a current of chlorine gas, free, or almost free, from air. The volatilized or sublimed mass which results is treated with hot water, with or without the addition of nitric or hydrochloric acid. For the recovery of stannic chloride from wolfram ores the sublimate is heated with hot water and hydrochloric acid, and the resulting soln. of stannic chloride is separated from the precipitated tungstic acid. The process may be made cyclic by heating the mixture of chlorides obtained in a current of dry air and using the chlorine thus recovered for the treatment of further quantities of ore. In a volatilization process devised by P. Jannasch and R. Leiste, the ore is heated in a current of the vapour of carbon tetrachloride, and the tungsten chlorides distilling over are decomposed by mineral acids. F. L. Hahn and W. Franke heated the tungstate with carbon tetrachloride under press. at 250° to 300°, and extracted the mass with acid.

The extraction of tungsten trioxide from wolframite by electrolysis.—R. E. Pearson and co-workers suggested the following process, but it has not been developed industrially. The tungsten ore, or waste-products containing that element are mixed with carbonaceous matter, and ground and mixed to a paste with sulphuric acid, and the mixture is placed on a lead plate which forms the anode of an electrolytic cell containing dil. sulphuric acid. On passing a current through the cell the basic impurities, *e.g.*, iron, manganese, calcium or sodium oxides, in the material on the anode pass into soln., leaving a residue of tungsten or molybdenum oxides. Alternatively the anode may consist of nickel or a nickel alloy, and the electrolyte of caustic soda, whereby soluble sodium tungstate or molybdate is formed and the foreign metals are left as anode slime.

The purification of tungsten trioxide.—The crude tungsten trioxide or sodium tungstate, prepared by these methods, may contain up to 2 per cent. of impurities, the nature of which depends on the ore and the method of extraction. The more common impurities are silica and oxides or salts of iron, manganese, calcium, titanium, tin, and molybdenum. The purity of the metal finally obtained depends largely on the purity of the oxide from which it is reduced. Ductile tungsten, and the tungsten employed for lamp filaments, and thermionic valves must be of a high degree of purity. Tungsten with 0·1 per cent. of iron is almost unworkable for ductile tungsten because of its brittleness. It is comparatively easy to reduce the total impurities to from 0·1 to 0·5 per cent., but elaborate processes are required for a higher degree of purity. When precipitation by an acid is employed as a means of purification, it is advisable to avoid colloidal precipitates because they are very liable to absorb impurities. Colloidal precipitation is favoured by the use of cold, dil. soln. ; conc. soln. are preferable. The subject was studied by L. Moser and J. Ehrlich.[5] The best results are obtained by running the tungstate soln. into the boiling acid ; rapid mixing favours the production of a coarse-grained precipitate. If cold hydrochloric acid of sp. gr. 1·19 is added drop by drop to a cold soln. of the tungstate, the precipitate first formed passes into the colloidal state as more acid is added; and the colloid is coagulated on boiling. If nitric acid be employed, the precipitate does not pass into the colloidal state. The washed precipitate produced by hydrochloric acid is fairly soluble in nitric acid, but the precipitate produced by nitric acid is scarcely soluble in hydrochloric acid. Sulphuric acid stands between nitric and hydrochloric acids in that the precipitate first formed is partly redissolved on adding more acid. If increasing amounts of acetic acid are added to sodium tungstate before adding hydrochloric acid, the initial precipitation does not occur until increasing amounts of hydrochloric acid are added, and the precipitate dissolves more quickly on adding more acid. However, the addition of 5 c.c. of acetic acid to 2 c.c. of a soln. of sodium tungstate gives a precipitate which is not soluble in hydrochloric acid. If tungstic acid be precipitated from sodium tungstate by hydrochloric acid, and allowed to stand, the precipitate is at first white and colloidal, it then becomes yellow and insoluble on the further addition of hydrochloric acid. The precipitated tungsten trioxide always carries down with it some of the salts dissolved in the mother-liquor. Thus, if 0·2 per cent. of iron is present in the soln. of ammonium tungstate run into boiling hydrochloric acid, the precipitate may contain 0·05 per cent. of ferric chloride; and tungstic acid precipitated from sodium tungstate by hydrochloric acid contains from 0·1 to 0·3 per cent. of sodium chloride. These impurities can to some extent be removed by washing with water; but the tungstic acid then becomes colloidal and filtration is impracticable. Washing with water containing 10 per cent. of hydrochloric or nitric acid, prevents the peptization of the tungstic acid; but even then it is not possible to completely remove the soluble impurities—0·09 per cent. of ferric oxide, and 0·06 per cent. of calcium oxide, as well as traces of titanium and molybdenum may be present. The precipitation is carried out in wooden vats or pots of vitreous silica. The sodium tungstate obtained from wolframite is sometimes purified by converting it into calcium tungstate by adding an excess of a soln. of calcium chloride of sp. gr. 1·16, and the washed precipitate is treated with boiling hydrochloric acid of sp. gr. 1·10. The process was described by C. H. Jones, who obtained a sample with 99·53 per cent. WO_3 by this means.

Hydrated tungsten trioxide readily dissolves in aq. ammonia, if it has not been dried at too high a temp., it is markedly less soluble if dried over 170°, and is practically insoluble if heated above 500°. Tungsten trioxide was purified by J. Persoz, F. A. Bernoulli, and A. Riche by dissolving it in aq. ammonia, and again precipitating it with acid. Several repetitions of the process are needed for a product of a high degree of purity. If the ammoniacal soln. of the tungsten trioxide is allowed to stand for some hours and then filtered, the impurity, iron, may pass into soln. The soln. is evaporated in order to obtain white crystals of ammonium paratungstate; these are washed with cold water and dried. One crystallization may not suffice for the removal of iron. The paratungstate, being insoluble in water, is decomposed by boiling with 40 per cent. nitric or hydrochloric acid, and the hydrated tungsten trioxide is dissolved in aq. ammonia and recrystallized as before. The crystallization may be modified by adding sodium or potassium hydroxide to the soln. of ammonium tungstate, when crystals of the complex salt $2R_2O.3(NH_4)_2O.12WO_3.15H_2O$ are obtained. The crystals can be decomposed by dissolving them in soda-lye, the ammonia driven off by heat, and the alkali tungstate soln. run into boiling acid. This modification gives tungsten trioxide free from iron, but it contains 0·1 to 0·3 per cent. of alkali chloride. E. F. Smith and F. F. Exner digested ammonium tungstate with nitric acid (1 : 1) and a little hydrochloric acid; and dissolved the thoroughly washed product in aq. ammonia. The soln. deposited crystals of ammonium paratungstate. After several repetitions of the process, the salt was digested with nitric acid; evaporated to dryness; and ignited. The oxide can also be purified by conversion into the oxychloride, and treatment with acid—O. Ruff, M. E. Pennington and E. F. Smith, and C. Friedheim and R. E. Meyer.

J. Waddell purified tungsten trioxide by fusing the crude oxide with potassium hydrosulphate; and dissolving the cold cake in water to remove the silica. The filtered soln. was fractionally precipitated by adding mercurous nitrate. The first fractions were treated with aqua regia, and the resulting hydrated tungsten trioxide fused with sodium carbonate. The cold mass was dissolved in water, mixed with enough tartaric acid to prevent precipitation when the soln. was acidified with hydrochloric acid. A current of hydrogen sulphide precipitates the molybdenum but not the tungsten. The filtered liquid was then boiled with an excess of conc. hydrochloric acid to precipitate the hydrated tungsten trioxide.

R. E. Pearson and co-workers described an electrolytic process of reducing the oxide—*vide* molybdenum. According to C. H. Fischer, metals which form insoluble sulphates can be removed by dissolving the crude tungsten trioxide in about twice its weight of fused potassium hydroxide mixed with lime; extracting the cold mass with water; and treating the soln. with a large excess of ammonium sulphide to precipitate iron, zinc, etc. The tungsten remains in soln. as polysulphide; it is precipitated as sulphide by adding hydrochloric acid; the precipitate is dried and oxidized by roasting, and the tungsten trioxide, thus formed, is purified by dissolving in potassium hydroxide soln. and reprecipitating with hydrochloric acid. Phosphorus and arsenic can be removed from the soln. of sodium tungstate as ammonium magnesium phosphate and arsenate by oxidizing the soln. with sodium hypochlorite; adding magnesium chloride; boiling the liquid; and adding ammonia and ammonium chloride in excess.

Some work has been done on the separation of molybdenum and tungsten. One series of processes is based on the fact observed by H. Rose.[6] When tartaric acid is added to the sulphuric acid soln. of the alkali salts, and hydrogen sulphide passed into the liquid, the molybdenum is precipitated as sulphide, while the tungsten sulphide is kept in soln. by the tartaric acid (J. Lefort, and J. Waddell). In another series, warm sulphuric acid of sp. gr. 1·378 dissolves the molybdenum from a mixture of the freshly precipitated molybdenum and tungsten trioxides (E. D. Desi, M. J. Ruegenberg and E. F. Smith, and W. Hommel). In a third series, if dry hydrogen chloride be passed over the mixed oxides at 250°–270°, the molybdenum oxychloride, $MoO_3.2HCl$, is alone volatilized (E. Péchard, and H. Debray). In a fourth series, the tungsten is precipitated as pentoxide when a soln. of stannous chloride is added to a boiling soln. of sodium tungstate and molybdate. The molybdenum remains in soln. (B. Mdivani, and E. E. Marbaker). Sodium tungstate free from molybdenum was prepared in the following manner by C. Friedheim and R. Meyer:

> Sodium tungstate, prepared in the usual way, is dissolved in cold water, and to the sat. soln. hydrochloric acid is added until the reaction is only feebly alkaline; the paratungstate thus obtained is crystallized out, and once recrystallized. One half of it is dissolved in boiling water, and hydrochloric and a little nitric acid added; hydrated tungstic acid is precipitated. This is washed thoroughly with hot water and added to a boiling soln. of the other half of the paratungstate, until a portion no longer gives a precipitate with hydrochloric acid. The bulk of the soln. is then filtered, hydrochloric acid is added, and the soln. is boiled and repeatedly sat. with hydrogen sulphide. This precipitates the molybdenum as sulphide, whilst the metatungstate is not attacked. The soln. is filtered, concentrated, oxidized with a few drops of bromine water, and neutralized with soda; pure sodium paratungstate can then be obtained from it by crystallization.

REFERENCES.

[1] E. Skewes, *Eng. Min. Journ.*, **76**. 424, 1903; E. Walker, *ib.*, **83**. 941, 1907; F. Dietzsch, *ib.*, **83**. 112, 1907; *Trans. Inst. Min. Met.*, **15**. 2, 1906; E. M. Lefroy, *ib.*, **25**. 82, 1915; A. Treloar and G. Johnson, *ib.*, **17**. 137, 1907; *Elektrochem. Zeit.*, **16**. 10, 1907; Anon., *Eng. Min. Journ.*, **86**. 573, 1908; **90**. 1058, 1910; **104**. 162, 741, 925, 1917; V. G. Hills, *ib.*, **102**. 126, 1916; *Proc. Colorado Scient. Soc.*, **9**. 135, 1909; **10**. 203, 1902; *Min. World*, **30**. 1021, 1909; *Min. Eng. World*, **38**. 443, 1913; *Min. Scient. Press.*, **106**. 448, 1913; R. D. George, *Eng. Min. Journ.*, **87**. 1055, 1909; F. A. Vogel, *ib.*, **99**. 287, 1915; J. F. Magee, *ib.*, **101**. 717, 1916; A. Grossberg, *ib.*, **102**. 139, 1916; Metallwerk Plansee Gesellschaft, *Brit. Pat. No.* 269947, 1926; H. R. von Wagenen, *Bull. Colorado School Mines*, **3**. 138, 1906; *Chem. Eng.*, **4**. 217, 284, 1906; *Min. Mag.*, **13**. 327, 1906; Anon., *ib.*, **6**. 44, 1912; **8**. 165, 1913; M. T. Taylor, *ib.*, **12**. 351, 1915; S. L. Terrell,

Min. Journ., **83**. 714, 1908; O. Falkenberg, *ib.*, **102**. 815, 1913; Anon., *ib.*, **110**. 532, 1915; S. J. Truscott, *Report of the Department of Scientific Industrial Research*, London, 1922; A. W. Gregory, *Brit. Pat. No.* 251527, 1925; H. H. Goe and S. W. French, *Min. Science*, **58**. 9, 1908; C. H. Paddock, *ib.*, **62**. 172, 1910; H. Lavers, *Proc. Australian Inst. Min. Met.*, 101, 1921; P. B. McDonald, *Mining Scient. Press.*, **112**. 40, 1916; H. E. Wood, *Proc. Colorado Scient. Soc.*, **9**. 154, 1909; *Min. World*, **30**. 968, 1909; T. Sington, *Eng. Min. Journ.*, **109**. 879, 1920; H. C. Parmlee, *Canadian Min. Journ.*, **32**. 458, 1911; *Met. Chem. Engg.*, **9**. 341, 409, 1911; **14**. 301, 1916; Anon., *ib.*, **14**. 559, 1916; **17**. 73, 207, 1917; S. Fischer, *ib.*, **16**. 559, 1917; **17**. 73, 1917; W. A. Longbottom, *Australian Min. Eng. Rev.*, **3**. 200, 1911; F. Freise, *Oesterr. Zeit. Berg. Hütt.*, **59**. 284, 1911; *Metall Erz*, **11**. 573, 587, 1914; J. M. Hill, *Bull. U.S. Geol. Sur.*, 648, 1916; M. Russell, *Queensland Govt. Min. Journ.*, **13**. 116, 1912; G. M. Dyson, *Chem. Age*, **16**. 33, 1927; H. B. Pickerings, *Min. Eng. World*, **37**. 60, 1912; W. A. Scott, *ib.*, **45**. 697, 1916; J. G. Hibbs, *ib.*, **44**. 953, 1915; F. L. Miner, *Min. Eng. World*, **44**. 1078, 1916; C. W. Gudgeon, *ib.*, **40**. 49, 1914; *Australian Min. Standard*, **50**. 409, 1914; R. W. Gannet, *Econ. Geol.*, **14**. 68, 1919; *Mining Mag.*, **20**. 311, 1919; G. W. Sears, *School Science*, **18**. 145, 1918; E. Ackermann, *Journ. Mines Met.*, **1**. 162, 1913; F. A. Savage, *Compressed Air Mag.*, **21**. 787, 1915; Anon., *Mex. Min. Journ.*, **19**. 92, 1915; A. J. Robertson, *Bull. Western Australian Geol. Sur.*, 64, 1916; R. R. Goodrich and H. E. Holden, *Journ. Amer. Inst. Min. Eng.*, **58**. 224, 1917; P. B. McDonald, *Min. Scient. Press.*, **112**. 40, 757, 1916; E. H. Leslie, *ib.*, **113**. 353, 1916; H. Fleck, *ib.*, **112**. 156, 1916; J. P. Bonardi, *Journ. Franklin Inst.*, **189**. 47, 1920; J. P. Bonardi and J. C. Williams, *Bull. U.S. Bur. Mines*, 187, 1921; J. F. L. Vogel, *B.A. Rep.*, 353, 1920; *Engg.*, **110**. 415, 1920; C. H. Jones, *Chem. Met. Engg.*, **22**. 9, 1920; O. H. F. Heizer, *Information Circ. U.S. Bur. Mines*, 6280, 1930; W. H. Coghill, *Tech. Paper U.S. Bur. Mines*, 456, 1929.

[2] A. E. Nordenskjöld, *Oefvers. Akad. Stockholm*, **17**. 439, 1860; *Pogg. Ann.*, **114**. 612, 1861; G. Gin, *Oesterr. Zeit. Berg. Hütt.*, **55**. 81, 1907; *Trans. Amer. Electrochem. Soc.*, **13**. 481, 1908; P. Schwarzkopf, *U.S. Pat. No.* 1629004, 1927.

[3] E. R. Schneider, *Pogg. Ann.*, **93**. 474, 1854; *Journ. prakt. Chem.*, (1), **50**. 154, 321, 1850; B. Franz, *ib.*, (2), **4**. 238, 1871; J. B. von Borck, *ib.*, (1), **54**. 254, 1851; *Oefvers. Akad. Förh.*, **8**. 147, 1851; W. Lotz, *Liebig's Ann.*, **91**. 51, 1854; *Journ. prakt. Chem.*, (1), **63**. 209, 1854; *Ann. Chim. Phys.*, (3), **43**. 246, 1855; A. Riche, *ib.*, (3), **50**. 33, 1857; J. Persoz, *ib.*, (4), **1**. 97, 1864; J. C. G. de Marignac, *Arch. Sciences Genève*, (2), **20**. 5, 1864; *Compt. Rend.*, **58**. 809, 1864; *Recherches sur le tungstène et ses composés*, Paris, 1857; *Ann. Chim. Phys.*, (3), **69**. 12, 1863; J. B. A. Dumas, *ib.*, (3), **55**. 144, 1859; K. Anjow, *Brit. Pat. No.* 241399, 1924; E. Zettnow, *Pogg. Ann.*, **130**. 16, 241, 1867; L. Weiss, *Zeit. anorg. Chem.*, **65**. 279, 1910; J. Philipp in A. W. Hofmann, *Bericht über die Entwickelung der chemischen Industrie*, Braunschweig, **1**. 744, 1875; K. Anjow, *U.S. Pat. No.* 1483567, 1924.

[4] J. B. Richter, *Ueber die neueren Gegenstände der Chymie*, Breslau, **1**. 45, 1791; **10**. 148, 1802; C. F. Bucholz, *Schweigger's Journ.*, **3**. 1, 1811; J. J. Berzelius, *ib.*, **16**. 476, 1816; *Ann. Phil.*, **3**. 245, 1814; *Ann. Chim. Phys.*, (2), **17**. 13, 1821; *Pogg. Ann.*, **4**. 147, 1825; **8**. 147, 267, 1826; E. Zettnow, *ib.*, **130**. 45, 1867; F. A. Bernoulli, *ib.*, **111**. 573, 1860; *Chem. News*, **5**. 116, 1862; F. Wöhler, *Pogg. Ann.*, **2**. 345, 1824; *Quart. Journ. Science*, **20**. 177, 1826; *Phil. Mag.*, **66**. 263 1825; *Nachr. Gött.*, 35, 1850; *Liebig's Ann.*, **73**. 190, 1850; **77**. 262, 1851; *Ann. Chim. Phys.*, (2), **29**. 43, 1823; (3), **29**. 187, 1850; A. Riche, *ib.*, (3), **50**. 33, 1857; J. C. G. de Marignac, *ib.*, (4), **3**. 12, 1864; *Arch. Sciences Genève*, (2), **20**. 5, 1864; *Compt. Rend.*, **58**. 809, 1864; F. Jean, *ib.*, **81**. 95, 1875; *Bull. Soc. Chim.*, (2), **25**. 65, 1876; *Ann. Chim. Anal. Appl.*, **9**. 321, 1875; L. Mayer, *Baumhartner's Zeit. Phys.*, **5**. 221, 1837; N. T. Gordon and A. F. Spring, *Journ. Ind. Eng. Chem.*, **16**. 555, 1924; R. Oxland, *Brit. Pat. No.* 11848, 1847; 3114, 1857; A. K. Huntington, *ib.*, 222, 1884; G. C. Wittstein, *Repert. Pharm.*, **73**. 82, 1841; J. B. von Borck, *Oefvers. Akad. Förh.*, **8**., 147, 1851; *Journ. prakt. Chem.*, (1), 54, 254, 1851; E. F. Anthon, *ib.*, (1), **8**. 399, 1836; (1), **9**. 6, 337, 1836; C. Scheibler, *Chem. News*, **6**. 181, 1862; *Journ. prakt. Chem.*, (1), **83**. 273, 1860; B. Franz, *ib.*, (2), **4**. 238, 1871; R. Derenbach, *Beiträge zur Kenntnis des Wolframs und seiner Legierungen mit Eisen*, Würzburg, 1892; K. Christl, *Dingler's Journ.*, **124**. 398, 1852; J. Philipp in A. W. Hofmann, *Bericht über die Entwickelung der chemischen Industrie*, Braunschweig, **1**. 744, 1875; C. H. Jones, *Chem. Met. Engg.*, **22**. 9, 1920; W. B. Gero and C. V. Iredell, *ib.*, **35**. 412, 1928; J. B. Ekeley and W. B. Stoddard, *Brit. Pat. No.* 122051, 1918; General Electric Co., *ib.*, 189873, 1921; W. H. Dyson and L. Aitchison, *ib.*, 176729, 1920; 176428, 1921; O. J. Stannard, *ib.*, 134891, 1921; R. E. Pearson, E. N. Craig and Durelco, Ltd., *ib.*, 185842, 1921; L. Weiss, *Zeit. anorg. Chem.*, **65**. 279, 1910; G. Gin, *Oesterr. Zeit. Berg. Hütt.*, **55**. 81, 1907; *Trans. Amer. Electrochem. Soc.*, **13**. 481, 1908; E. K. Jenckes, *ib.*, **51**. 299, 1927; G. A. Hempel, *German Pat., D.R.P.* 221062, 1907; H. Bradenburg and A. Weyland, *ib.*, 149555, 1902; F. E. Clotten, *ib.*, 141811, 1902; Elektrochemische Fabrik Kempen a.Rh., *ib.*, 149556, 1902; P. Jannasch and R. Leiste, *ib.*, 266973, 1914; *Journ. prakt. Chem.*, (2), **88**. 129, 1913; R. Leiste, *Ueber eine neue analytische Methode zur Bestimmung der Phosphate und Wolframate mittelst Kohlenstofftetrachlorid*, Heidelberg, 1910; F. L. Hahn and W. Franke, *German Pat., D.R.P.* 437561, 1925; G. Bessa, *L'Ind. Chim.*, **9**. 2, 1922; *Chem. Trade Journ.*, **70**. 199, 1922; W. B. Stoddard and I. Hochstadter, *U.S. Pat. No.* 1652646, 1927; R. W. Stimson, *Brit. Pat. No.* 320845, 1928.

[5] L. Moser and J. Ehrlich, *Edelerden und Erze*, **3**. 49, 65, 1922; C. H. Jones, *Chem. Met. Engg.*, **22**. 9, 1920; *Metal Ind.*, **16**. 107, 1920; F. A. Bernoulli, *Pogg. Ann.*, **111**. 590, 1860; *Chem. News*, **5**. 116, 1862; J. Persoz, *Ann. Chim. Phys.*, (3), **1**. 97, 1864; A. Riche, *ib.*, (3), **50**.

33, 1857; L. P. Wyman, *The Purification of Tungstic Acid*, Philadelphia, 1902; J. Waddell, *Amer. Chem. Journ.*, **8**. 280, 1886; *Chem. News*, **55**. 101, 112, 1887; *Trans. Roy. Soc. Edin.*, **33**. 1, 1889; *Zeit. phys. Chem.*, **3**. 491, 1889; R. E. Pearson, E. N. Craig and Durelco, Ltd., *Brit. Pat. No.* 181837, 1921; C. H. Fischer, *ib.*, 17603, 1912; O. Ruff, *Zeit. angew. Chem.*, **25**. 1889, 1912; M. E. Pennington and E. F. Smith, *Zeit. anorg. Chem.*, **8**. 198, 1895; C. Friedheim and R. E. Meyer, *ib.*, **1**. 76, 1892; E. F. Smith and F. F. Exner, *Proc. Amer. Phil. Soc.*, **43**. 123, 1904; *Chem. News*, **90**. 37, 49, 66, 1904; *Journ. Amer. Chem. Soc.*, **26**. 1082, 1904; F. Filsinger, *Deut. Ind.*, **1**. 246, 1878.

[6] H. Rose, *Handbuch der analytischen Chemie*, Leipzig, **2**. 358, 1871; C. Friedheim and R. Meyer, *Zeit. anorg. Chem.*, **1**. 76, 1892; E. Péchard, *ib.*, **1**. 262, 1892; *Chem. News*, **65**. 89, 1892; *Compt. Rend.*, **114**. 173, 1892; H. Traube, *Neues Jahrb. Min. B.B.*, **7**. 232, 1890; P. Jannasch and W. Bettges, *Ber.*, **37**. 2219, 1904; J. Lefort, *Ann. Chim. Phys.*, (5), **9**. 93, 1877; J. F. John, *Chemisches Laboratorium*, Berlin, 305, 1808; C. H. Pfaff, *Handbuch der analytischen Chemie*, Altona, **2**. 501, 1822; J. Waddell, *Amer. Chem. Journ.*, **8**. 280, 1886; *Trans. Roy. Soc. Edin.*, **33**. 1, 1889; *Chem. News*, **55**. 101, 112, 1887; H. Brearley, *ib.*, **79**. 64, 1899; H. Brearley and F. Ibbotson, *ib.*, **80**. 294, 1899; **81**. 13, 1900; E. F. Smith and F. F. Exner, *ib.*, **90**. 37, 1904; *Journ. Amer. Chem. Soc.*, **26**. 1082, 1904; E. D. Desi, *ib.*, **19**. 213, 1897; M. J. Ruegenberg and E. F. Smith, *Chem. News*, **83**. 5, 1901; *Journ. Amer. Chem. Soc.*, **22**. 772, 520, 1895; M. E. Pennington and E. F. Smith, *Zeit. anorg. Chem.*, **8**. 198, 1895; E. F. Smith and V. Oberholtzer, *ib.*, **4**. 236, 1893; *Journ. Amer. Chem. Soc.*, **15**. 206, 1983; W. Hommel, *Ueber die quantitative Trennung von Wolfram und Molybdän*, Zürich, 1902; E. E. Marbaker, *The Separation of Tungsten from Molybdenum*, Philadelphia, 1914; *Journ. Amer. Chem. Soc.*, **37**. 86, 1915; H. Mennicke, *Die quantitativen untersuchungensmethoden des Molybdaens, Vanadiums und Wolframs*, Berlin, 1913; H. Debray, *Compt. Rend.*, **46**. 1101, 1858; J. B. Ekeley and W. B. Stoddard, *U.S. Pat. No.* 1399705, 1921; B. Mdivani, *Bull. Soc. Chim.*, (4), **9**. 122, 1911; C. Reichard, *Chem. Ztg.*, **26**. 4, 1903; I. Koppel, *ib.*, **48**. 801, 1924.

§ 4. The Preparation of Tungsten

For the preparation of the metal of a high degree of purity, the oxide is reduced by heating it in a current of *hydrogen*. This method was used by J. J. Berzelius,[1] F. Wöhler, F. Jean, J. Waddell, W. Majert, C. W. Davis, C. W. Siemens and A. K. Huntington, C. W. Blake, T. Sington, G. Bessa, L. R. Pratt, C. M. Johnson, H. N. Warren, E. R. Schneider, J. B. von Borck, A. Riche, E. Zettnow, R. F. Marchand, Badische Anilin- und Sodafabrik, P. Schwarzkopf, E. Ruhstrat, C. H. Jones, H. E. Roscoe, J. Schilling, E. Thomson, C. W. Davis, J. Philipp, V. I. Spitzin, A. Pacz, etc. G. Chaudron determined the conditions of equilibrium in the system: $WO_3+3H_2 \rightleftharpoons W+3H_2O$, between 600° and 1100°. The trioxide passes through various intermediate stages before it is reduced to metal; there is yellow WO_3; deep blue W_2O_5; and chocolate-brown WO_2. If the reduction is stopped at intervals, these changes in colour succeed one another as the reduction proceeds. Thus, at 400°, the greenish-blue product has the approximate composition $WO_3+W_2O_5$; at 500°, intense blue W_2O_5 is formed; at 550°, dark blue W_2O_5; at 575°, purple-brown $W_2O_5+WO_2$; at 600°, chocolate-brown WO_2; at 650°, brownish-black WO_2+W; at 700°, greyish-black W; at 800°, grey W; at 900°, metallic grey W; and at 1000°, coarse metallic W. The observed values of the constant $K_p=[H_2O]/[H_2]$, corresponded with the reactions: $H_2+2WO_3 \rightleftharpoons W_2O_5+H_2O$, for which J. A. M. van Liempt gave $\log K_1=-2468T^{-1}+3{\cdot}15$; $H_2+W_2O_5 \rightleftharpoons 2WO_2+H_2O$, for which $\log K_2=-817T^{-1}+0{\cdot}88$; and $2H_2+WO_2 \rightleftharpoons W+2H_2O$, for which $\log K_3 =-111T^{-1}+0{\cdot}845$. G. Chaudron's values of log K and T^{-1} are plotted in Fig. 2. The results were confirmed by L. Wöhler and co-workers—*vide infra*. L. Wöhler and R. Günther gave for $WO_3 \rightarrow W_2O_5$, $\log K_1=-1375T^{-1}+2{\cdot}235$; for $W_2O_5 \rightarrow WO_2$, $\log K_2=-1000T^{-1}+1{\cdot}218$; and for $WO_2 \rightarrow W$, $\log K_3=-1904T^{-1}+1{\cdot}554$. W. Reinders and A. W. Vervloet could not obtain satisfactory values for K_1 because

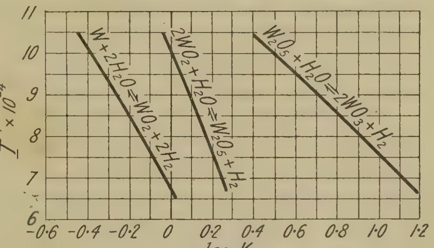


FIG. 2.—Equilibrium between Water, Hydrogen, Tungsten, and its Oxides.

the composition of the blue oxide obtained varied from W : O=1 : 2·20 to 1 : 2·95. H. Alterthum and F. Koref studied this subject—*vide infra*, the individual oxides. G. Chaudron found that if the equilibrium curves are extrapolated, 1 and 2 will intersect at a lower temp., and 2 and 3 at higher temp. Hence, above and below these points there must be equilibria represented by $W_2O_5+5H_2\rightleftharpoons 2W+5H_2O$, and $WO_3+H_2\rightleftharpoons WO_2+H_2O$. At 900°, WO_2 is stable in a mixture of 40 to 55 per cent. of hydrogen, and 60 to 45 per cent. of steam, while W_2O_5 is stable in a mixture of 12 per cent. of hydrogen and 88 per cent. of steam. J. A. M. van Liempt prepared these two oxides by passing hydrogen through water at 85° and 97° respectively, in order to obtain the correct proportion of steam in the gas, and then over a thin layer of tungsten trioxide. If the steam be removed continuously from the sphere of the reaction, the tungsten trioxide is reduced to metal provided the temp. is at least 700°. At lower temp., the time required is too long to be practicable. G. A. Meerson studied this subject and found that the size of the crystals of the trioxide does not influence the size of the crystals of tungsten.

F. Wöhler, and W. Majert reduced red-hot acid potassium tungstate in a current of hydrogen, and washed out the normal tungstate by boiling alkali-lye. E. Defacqz obtained crystals of the metal by heating tungsten disulphide in a current of dry hydrogen; L. von Uslar, by passing a mixture of hydrogen and the vapour of the oxychloride $WOCl_4$ or WO_2Cl_2 through a red-hot tube; H. E. Roscoe, by passing a mixture of hydrogen and the vapour of the chloride WCl_4 or WCl_5 through a tube at about 420°; and F. Wöhler, by passing hydrogen over the amide. Other reducing gases may be used: thus, C. W. Davis found that a 2 hrs.' reduction by *gasoline* vapour at 1080° yielded a product with 98 per cent. tungsten; J. J. Berzelius found that tungsten trioxide, heated with sodium carbonate on charcoal in the inner blowpipe flame, is reduced to metal; and E. D. Clarke reported that he obtained a copper-coloured metal by heating tungsten trioxide before the oxy-hydrogen blowpipe flame.

J. L. Gay Lussac and L. J. Thénard reduced tungsten trioxide to tungsten by heating it with *potassium* or *sodium*. E. Zettnow heated a mixture of tungsten trioxide and sodium under a layer of fused sodium chloride, in an iron crucible, and extracted the cold mass with water, and dil. hydrochloric acid to remove the alkali salts and iron. A. Riche reduced tungsten hexachloride to metal by means of sodium; and J. W. Marden used a modification of the process. A. Burger, A. S. Cachemaille, and H. Kuzel and E. Wedekind reduced tungsten trioxide by heating it in an evacuated tube in the vapour of *calcium*; and washing out the calcium oxide by dil. nitric acid. K. Kuzel and E. Wedekind used this process. L. Weiss and A. Martin found that calcium and L. Weiss and O. Aichel that *mischmetall* are not satisfactory reducing agents. L. Weiss and A. Martin used *magnesium* as a reducing agent; and H. Wright, *tin*. S. M. Delépine reduced tungsten trioxide to metal by means of powdered *zinc* at a red-heat; and washing out the zinc oxide with hydrochloric acid, and the unchanged trioxide by dil. alkali-lye. L. Weiss and A. Martin obtained 99·8 per cent. tungsten by this means. E. Straub obtained alloys by passing the vapour of the required metal over heated tungsten trioxide. H. Goldschmidt found that tungsten trioxide is easily reduced by *aluminium* in the thermite process. An intimate mixture of the trioxide and powdered aluminium, contained in a crucible, can be ignited by a fuse of sodium or barium dioxide mixed with some magnesium powder. As a result, an alloy of aluminium-tungsten is formed and it dissolves in the tungsten. The excess of tungsten trioxide forms an aluminium tungstate, and goes into the slag. O. Voigtländer heated the mixture of tungsten trioxide and aluminium so that after the reduction the temp. is high enough to keep the tungsten in a molten state. The aluminium reduction process was discussed by H. Goldschmidt and C. Vautin, J. W. Marden, G. A. Percival, C. R. Schroeder, H. Lohmann, G. Bessa, W. C. Blake, J. L. F. Vogel, N. Branoic, A. Martin, and F. Kupelwieser. K. Metzger said that the yield is poor. L. Weiss and A. Martin found that the product has 93·36 per cent.

of tungsten, 1·75 per cent. of silicon, 3·68 per cent. of aluminium, and 2·18 per cent. of calcium. A. Stavenhagen used one-third the vol. of liquid air to ignite the mixture of tungsten trioxide and aluminium. W. Prandtl and B. Bleyer recommended a mixture of calcium and aluminium in place of aluminium alone. A. Stavenhagen and E. Schuchard obtained alloys by reducing a mixture of the oxides with aluminium. B. Neumann reduced the oxide with *silicon;* and F. M. Becket found that tungsten trioxide can be reduced by silicon or *boron* when the mixture is heated in an electric furnace.

When tungsten trioxide first attracted attention, it was reduced to a metal by heating it with *carbon* or carbonaceous matter. J. J. and F. de Elhuyar, L. N. Vauquelin and L. Hecht, C. Hatchett, W. Allen and A. Aikin, G. Bessa, D. J. Giles, A. Ruprecht, H. W. Hutchin, and E. Zettnow used this method; while C. F. Bucholz, F. A. Bernoulli, and J. J. Berzelius thus obtained " tungsten " by heating a mixture of carbon and a tungstate. H. Krieg, and E. Defacqz obtained " tungsten " directly by heating a mixture of the tungstate ore and carbon. Slightly less than the theoretical proportion of carbon—coke, anthracite, coal, or charcoal—required for reducing the trioxide to tungsten and carbon monoxide, is intimately mixed with the powdered oxide. The mixture is charged into a crucible, which is then covered, and heated in a furnace. The metal remains as a fine grey powder mixed with coarser crystals, and undecomposed oxide. The coarse crystals are separated by washing out the fine particles which are added to the next charge. F. Filsinger heated a mixture of tungsten trioxide with 10 per cent. of wood-charcoal, and 2 to 3 per cent. of resin. The powdered metal is separated by levigation. It has not a high degree of purity; it contains 80 to 90 per cent. tungsten. At a temp. of 950°, M. R. Andrews and S. Dushman observed that tungsten unites with carbon, forming carbides which are stable up to 2400°; in consequence, tungsten obtained by reduction with carbon always contains some carbide. According to C. W. Davis, in order to obtain a satisfactory reduction of tungsten trioxide to tungsten, the material must be freed from water, which is best effected by a current of air at about 500°. On reducing the dried oxide with carbon, a blue or purple oxide is produced at 650° to 850°, a chocolate-brown mixture of oxides at 900° to 1050°, and metallic tungsten above 1050°. The proportion of carbon required for the reduction ranges from 1 : 10 to 1·6 : 10, according to the temp., time, and other conditions. Excess of carbon can be removed to a considerable extent by washing the product with water. C. J. Butterfield heated a mixture of scheelite and charcoal in a graphite crucible for 4 to 5 hrs. at 1100°–1200°. The reaction with calcium tungstate is symbolized: $CaWO_4+3C=W+CaO+3CO$; and with sodium tungstate: $Na_2WO_4+3C=W+Na_2O+3CO$. The cold mass was powdered, and the metal separated on a shaking table. The product was then washed with dil. hydrochloric acid. C. J. Head mixed finely ground sodium tungstate with ammonium-chloride—or any chloride of the iron or manganese group, and a suitable reducing agent—wood charcoal, anthracite, or preferably sawdust—and heated the mixture in a nichrome crucible at 850° to 950° for 3 to 5 hrs. until all the ammonia was expelled. The reaction is symbolized: $2NH_4Cl+Na_2WO_4+3C=2NH_3+2NaCl+H_2O+3CO+W$. The lower half of the charge is removed and heated to 1000° to 1150°, out of contact with air, whereby the tungsten trioxide is reduced to tungsten powder. The mass is quenched in water, and the insoluble tungsten washed in the usual way. The tungsten can be recovered as calcium tungstate by adding calcium chloride to the washing liquid; the ammonia is also recovered. H. Moissan reduced the oxide by sugar-charcoal in an electric arc furnace. The metal is readily fused in that furnace, but if the heat is not allowed actually to melt the tungsten, and the tungsten trioxide be in excess, the metal can be produced in a form almost free from carbon. The ingot so obtained is fused on the surface but the interior is porous; and the mass touches the carbon crucible only at a few points. Consequently, *le carbone du creuset n'intervient pas*, and the excess of tungsten trioxide is volatilized. G. Gin used a similar process, and added that there is a considerable loss of tungsten trioxide by volatilization. H. Lohmann found that if the metal be heated to near its m.p. in vacuo or in a current of neutral gas, any contained carbon is vaporized without oxidizing or reducing agents being present. E. D. Desi said that at a very high temp. *potassium cyanide* reduces tungsten trioxide to the silver-white metal. H. N. Warren, and R. Saxon reduced the oxide by heating it with *calcium carbide;* the Electric Furnaces and Smelters Ltd. reduced the oxide by a mixture of calcium carbide and silicide, or *ferrosilicon.* L. Kahlenberg and W. J. Trautmann observed that tungsten trioxide is not easily reduced when heated with *silicon;* and the tungstates of barium, lead, and sodium do not yield the free metal or silicide—excepting, perhaps, the case of barium tungstate. F. M. Becket used *silicon carbide* as reducing agent. J. N. Pring and W. Fielding found that tungsten hexachloride is reduced by carbon at 1000° to 1500°. A. E. van Arkel found that the thermal dissociation of a gaseous compound, and the precipitation of the metal on an incandescent filament is a superior method for making tungsten of a high degree of purity. F. Koref recommended heating a filament to 1000° in an atm. of tungsten hexachloride and hydrogen at about 12 mm. press.; and Philips Gloelampenfabriken heated single crystals of tungsten in an atm. of the hexachloride at 1200° to 2400°. In the one case the wire increased in volume. If an iron rod is used, N. Parravano and C. Mazzetti found that an alloy of tungsten and iron is formed. O. L. Mills made alloys of tungsten by fusing in an electric arc, a mixture of the compound of the metal with a mixture of tungsten oxide, tungsten, and tungsten carbide.

L. and H. H. Kahlenberg added zinc to a soln. of a tungstic acid or tungsten trioxide in fused sodium and potassium chlorides, and obtained a black powder of tungsten; the action of aluminium is faster than that of zinc; but iron produces no deposition of tungsten. J. Férée distilled mercury from the amalgam and obtained the finely-divided metal. G. Arrivant prepared 99·35 per cent. tungsten by treating a pulverized tungsten alloy, containing 55 per cent. of manganese, with hydrochloric acid. C. W. von Siemens and J. G. Halske heated an alloy of tungsten with some other metals electrically, in vacuo, and found that the foreign metals distilled off, leaving the tungsten behind.

Early in the nineteenth century, J. G. Children [2] reduced tungsten trioxide by means of an electric current; about the middle of the nineteenth century, M. Junot reduced tungsten electrolytically from a soln. of a tungstate in potassium cyanide and alkali hydroxide; and in 1867, E. Zettnow electrolyzed fused sodium tungstate and obtained a deposit of tungsten on the iron cathode. The metal has not been obtained satisfactorily by the electrolysis of aq. soln. of the tungstates. This fact would not have been anticipated from the ease with which chromium, a member of the same family of elements, can be deposited from aq. soln. E. F. Smith, and W. E. Koerner tried electrolyzing neutral and acidic soln. of sodium tungstate, and found that the liquid turns blue owing to the formation of the blue hemipentoxide which collects as a precipitate at the bottom of the cell; the brown dioxide may also be formed. No metal is deposited. O. Collenberg and K. Nilsson electrolyzed conc. oxalic acid soln. of potassium tungstate at 70° with various metal cathodes. They found that with a tin or lead cathode, the reduction does not go further than the hemipentoxide; while with platinum or mercury cathodes, the reduction does not proceed so far as the hemipentoxide. O. Collenberg and J. Backer failed with hydrochloric acid soln. as electrolytes; L. W. McCay and N. H. Furman failed with hydrochloric acid soln.; and A. Fischer, with an alcoholic soln. of tungsten hexachloride. The Wolframlampen A.G. patented the electrolysis of a soln. of pertungstic acid or its salts in aq. or organic solvents; and the electrolysis of soln. of the salts, say tungsten hexachloride, in suitable organic solvents, say acetone. The subject was discussed by D. B. Keyes and S. Swann. C. A. Mann and H. O. Halvorsen observed that the electrolysis of aq. soln., or of hydrochloric acid soln. with tungsten electrodes, gives a surface film of oxide which makes the tungsten passive and prevents further electrolysis. When a soln. of dry hydrogen chloride in dry alcohol is electrolyzed with a tungsten anode, tungsten chloride goes into soln., but only the brown oxide is deposited on the cathode. A soln. of hydrogen chloride in pyridine does not ionize enough to produce tungsten chloride, and no deposit is obtained on the cathode. A. Rosenheim and R. F. Bernhardi-Grisson found that with a graphite anode and platinum cathode with alcoholic hydrogen chloride soln. of tungsten trioxide, the reduction proceeds only as far as the quinquevalent stage ; and with hydrofluoric acid soln., and a mercury cathode, reduction proceeds as far as the quadrivalent stage. H. Leiser observed that no change occurs in the electrolysis of normal sodium tungstate, but with the metatungstate electrolytic reduction proceeds as far as the blue compound. L. and H. H. Kahlenberg obtained a good deposit by the electrolysis of a mixture of fused sodium and potassium chlorides if less than one part of tungsten trioxide to two parts of fused chlorides is present. R. E. Pearson and E. N. Craig said that tungsten is formed when a direct current is passed through a cell with pasty tungsten trioxide in the cathode chamber, and sulphuric acid as electrolyte. B. Neumann and H. Richter obtained small deposits of tungsten from soln. of the hexachloride in glycerol which forms a compound containing tungsten ions.

Better results have been obtained by the electrolysis of fused tungstates. J. A. M. van Liempt found that the alkali tungstates melt without decomposition between 750° and 950°, while the eutectic mixture of lithium, potassium, and sodium tungstates melts at about 400°. F. M. Jäger and B. Kapma found that the conductivity of the fused salt increases with temp. L. A. Hallopeau found that when molten lithium paratungstate at 1000° is electrolyzed at 3 amp. and 15 volts, the product, after extraction with hot water, conc. hydrochloric acid, and lithium hydroxide soln., consists of crystalline tungsten which is contaminated with more or less platinum derived from the electrodes. The opaque prismatic crystals have the acicular habit, and in some cases contain 99·64 per cent. tungsten. Iron electrodes cannot be used because that metal dissolves in the molten tungsten. J. A. M. van Liempt electrolyzed fused sodium tungstate at 950°, in a vitreous silica crucible, with a current density of 15 amp. per sq. cm. The yield was 80 per cent. of the theoretical. The tungsten is produced by the reduction of the molten tungstate by the nascent sodium liberated at the cathode : $6Na+5Na_2WO_4=W+4Na_4WO_5$. Pure tungsten is obtained so long as the mass remains neutral or weakly alkaline. If it becomes too strongly alkaline the tungsten redissolves. In acid fusions, reduction of W_2O_7 ions by the sodium occurs with the formation of " tungsten bronzes " of the type $M_2(WO_3)_n$. The electrical resistance of these " bronzes " decreases rapidly with rise of temp. owing to the gradual liberation of tungsten. The anode reaction is $WO_4''+Na_2WO_4=Na_2W_2O_7+0{\cdot}5O_2$. When unattackable electrodes are used in a cell without a diaphragm, the products of these electrode reactions react, making the mass alkaline : $4Na_4WO_5+3Na_2W_2O_7=10Na_2WO_4+Na_2O$. The electrolysis may be made continuous under these conditions by gradually adding tungsten trioxide. In the presence of WO_4'', a tungsten anode is oxidized, the oxide dissolving to keep the fused mass neutral. Tungsten may be deposited in an adhesive, polishable layer on copper, nickel, or cobalt by using these metals as cathodes in the electrolysis of fused acid tungstates at 1000°. Lithium acid tungstates give the best results. Repeated layers of tungsten may be thus deposited if the surface layers of " tungsten bronzes " are removed between each electrolysis. The tungsten is formed by the decomposition of " tungsten bronzes " primarily deposited. According to L. Weiss and A. Martin, tungsten trioxide may be readily electrolyzed if it be fused with cryolite, and a current of 250 amp. and 13 to 14 volts be employed. The globules of metal contain 96 per cent. of tungsten. In order to raise the temp. of the bath, alumina may be added, but the aluminium which is then liberated reacts with the tungsten trioxide, forming tungsten in a fine state of subdivision. In the electrolysis of fused barium tungstate with a current of 250 amp. at 20 volts, the resulting metal powder, after washing many times with dil. nitric acid, water, and aq. ammonia, contains 89·58 per cent. of tungsten, and 2·54 per cent. of barium. If barium chloride be also added to the electrolyte, 90·98 per cent. tungsten was obtained and it had 1·99 per cent. of barium. Another process was described by E. W. von Siemens and J. G. Halske. J. A. M. van Liempt coated metals with tungsten by placing a tungsten anode in a porcelain crucible containing lithium tungstate, and the body to be coated as cathode. A current density of 75 milliampères per sq. cm. is used at 0·08 volt. If the coating does not adhere readily to the metal, the metal is first coated with another suitable metal—*e.g.* iron is coated with copper. L. Andrieux obtained the metal by the electrolysis of fused borates.

C. A. Mann and H. O. Halvorsen obtained a deposit on iron when fused lithium chloride is used as an electrolyte, with a tungsten anode and an iron cathode; H. Mennicke also obtained a deposit with fused sodium and tungsten chlorides as electrolyte and a tungsten cathode. L. and H. H. Kahlenberg electrolyzed soln. of tungstic acid or tungsten trioxide in fused alkali chlorides, and in fused sodium tungstate, and obtained smooth deposits of tungsten. They said that the electrolysis of tungstic acid dissolved in a fused mixture of sodium and potassium chlorides yielded good deposits of very pure tungsten when the ratio of tungstic acid to fused chloride was less than 1 : 2; a blue crystalline tungsten bronze, $Na_2O.W_4O_{14}$, was obtained when the ratio was 1 : 1; a red bronze, $2Na_2O.W_5O_{13}$, when the ratio was 3 : 5; and a violet-bronze, when the ratio was 4 : 5. From soln. of tungstic acid in fused chlorides, zinc and aluminium liberated very finely-divided metallic tungsten, whereas iron had no action; excess of zinc or aluminium yielded alloys of these metals with tungsten. Nickel-tungsten alloys were obtained by electrolysis of mixtures of nickel chloride, alkali chloride, and tungstic acid. L. Andrieux obtained the metal by the electrolysis of a soln. of the trioxide in fused borate and fluoride. L. St. C. Broughall electrolyzed a soln. of a tungsten salt in liquid ammonia at a low temp. or high press. J. Férée obtained tungsten by the electrolysis of a hydrofluoric acid soln. of the trioxide, using a mercury cathode; and K. S. Jackson and co-workers found that best conditions are to use a $4·6N$-acid at 95°, and a current density of 0·65 to 1·0 amp. per sq. cm. Hydrochloric and sulphuric acids should not be present in the electrolyte.

According to J. J. Runner and M. L. Hartmann,[3] 90 per cent. of the tungsten extracted from ores is employed in the preparation of *ferrotungsten* containing 50 to 85 per cent. tungsten. R. M. Keeney described the preparation of the alloy by the reduction of tungsten ores by carbon in crucibles—*vide supra*—prior to the introduction of the electric furnace about 1900. The reduction of the ores by the aluminium thermite process—*vide supra*—has also been employed. A. J. Rossi reduced ferberite with aluminium in an electric furnace obtaining an alloy with 75·9 per cent. W; 21·4, Fe; 1·6, Si; 0·08, S; and 0·9, C. G. Gin produced ferrotungsten by reducing scheelite or artificial calcium tungstate by 20 per cent. ferrosilicon in an electric furnace having two contiguous hearths in series, with ferrosilicon electrodes, and an intermediate electrode of fused ferrosilicon. The scheelite is placed on the melted bath of ferrosilicon, and the silicon oxidizes at the expense of the tungsten trioxide, and forms a slag; the iron forms ferrotungsten. A common method of producing ferrotungsten is to reduce the ore wolframite, ferberite, and hubnerite in an electric furnace with carbon. The manganese either volatilizes or passes into the slag. The product usually contains more carbon than is desired in ferrotungsten for steel making, and it is therefore decarburized.

The decarburization process described by D. A. Lyon and co-workers, and R. M. Keeney involves heating the metal in the electric furnace in the presence of tungsten trioxide, hammer scale, or iron oxide. In this way, the carbon can be reduced to 0·15 per cent. The oxidation of carbon by iron oxide entails losses as iron tungstate, but this loss can be reduced by adding silica, which results in the formation of ferrous silicate. G. Gin recommended casting the carburized tungsten in the form of electrodes, which are used with a soft steel intermediate electrode. The bath above the metal is of tungsten oxide and magnesium aluminate. The electrodes melt, and their carbon is burnt out by the tungsten oxide. A. Lederer reduced the carbon content of tungsten from 2·5 to 0·04 per cent. by heating the metal in dry hydrogen to 1200° to 1300°; the Vereinigte Gluhlampen A.G. recommended using a mixture of hydrogen sulphide and hydrogen; the Zirkon Glühlampenwerke A.G. employed phospham; and E. W. von Siemens and J. G. Halske heated the metal electrically in acetic acid vapour. F. M. Becket dephosphorized the metal by feeding the solid metal in a finely-divided state on to the surface of a molten basic oxidizing bath—say scheelite and lime—at a temp. equal to or above the m.p. of the ferrotungsten. E. W. von Siemens and J. G. Halske discussed the removal of oxides from the metal.

Ductile tungsten.—In connection with the manufacture of incandescent filament lamps,[4] the good results with tantalum filaments stimulated the examination of the scarcer metals, and tungsten, in its turn, was tried. The tungsten produced at that time was so hard and brittle that, unlike tantalum, it could not be drawn into filaments. The filaments were therefore prepared by a process of squirting similar to that employed in preparing carbon filaments. The powdered metal mixed with some binding agent—gum, gelatine, a soln. of nitrocellulose in amyl acetate, pinene hydrochloride, etc.—was squirted through a die, dried, and heated. The tungsten powder was also mixed with cadmium amalgam, and after squirting through a die, the cadmium and mercury were removed by volatilization. The colloidal metal was also tried as a source of tungsten for manufacturing filaments. Here no binding agent is required. Filaments have also been made by the Wolframlampen A.G., and A. Just and F. Hanaman by introducing a glowing metal or carbon filament in an atm. of tungsten oxychloride, WO_2Cl_2 or $WOCl_4$, and an excess of hydrogen. Tungsten is thus deposited on the filaments—*e.g.* according to the conditions, the carbon may be wholly or partially replaced, $WO_2Cl_2+2C+H_2=2HCl+2CO+W$; or $WO_2Cl_2+3H_2=2HCl+2H_2O+W$—and the filament thus consists of a core of metal or carbon enclosed in a tube of tungsten.

The tungsten filaments prepared by these processes were strong and elastic, but were incapable of taking the slightest permanent set when cold, although they were ductile at a very high temp. The ductility of tungsten was shown by W. D. Coolidge[5] to be conditioned by the purity of the metal. According to O. Ruff, the metal must be entirely free from oxide; iron and nickel and non-metallic impurities like sulphur, and phosphorus must be entirely absent; and it should not contain more than about 0·1 per cent. of carbon. Before working, the metal should be sintered almost to the m.p. in order to obtain it in as dense a condition as possible. The British Thomson-Houston Co. obtained ductile tungsten by working a heated body of coherent tungsten so as to transform the metal by repeated rolling, hammering, swaging, or drawing into a form which shows a conchoidal fracture and ultimately becomes very fibrous. C. J. Smithells, and others have described the essential details of the process. The powder is first pressed into briquettes; this is then heated in hydrogen at 900° to 1050° to sinter the powder; then formed by heating it in hydrogen to nearly its m.p.; it is then worked into a rod by mechanical hammering called "swaging"; and after that it is drawn successively through smaller and smaller dies, at 400° to 650°, until the wire has the required diameter. The draw-plate is lubricated with a mixture of deflocculated graphite and water. The wires appear blue-black owing to the surface coating of oxide and graphite; and they are cleaned by being electrically heated to dull redness in an atm. of hydrogen; or by treating the wire with a hot soln. of soda-lye, sodium dioxide, hydrogen dioxide and ammonia.

P. Schwarzkopf and S. Burgstaller obtained ductile tungsten by the method indicated in connection with ductile molybdenum. The addition of less than one per cent. of thoria to the tungsten trioxide before the reduction was shown by Westinghouse Metallfaden-Glühlampenfabrik to make the product more ductile—possibly, according to Z. Jeffries, and F. A. Fahrenwald, by preventing recrystallization. The filaments in use are liable to recrystallize and revert to their original hard, brittle condition. This shows itself by irregular thickenings. A. Lederer said that the thickenings are longitudinal when a direct current is used, and with an alternating current there is a kind of sliding motion between adjacent parts of the filament which results in fracture. These defects are alleviated by using an alloy of tungsten with one of the rare metals instead of tungsten alone. The thorium oxide-tungsten filaments were studied by W. Geiss and J. A. M. van Liempt.

J. Férée [6] prepared pyrophoric tungsten by the distillation of mercury from tungsten amalgam. H. Kuzel obtained **colloidal tungsten** by treating it alternately with dil. soln. of acid and neutral reagents. 10 kgrms. of the metal were heated for 24 to 48 hrs. with 75 kgrms. of 15 per cent. hydrochloric acid, well agitated, decanted, and washed with distilled water, until some colloidal metal began to pass into the filtrate. The metal was then treated for 24 hrs. with 75 kgrms. of a one per cent. soln. of potassium cyanide, washed with distilled water, and heated with 75 kgrms. of a one per cent. soln. of ferrous sulphate. After washing to remove the iron salts, the residue is treated with a 2 per cent. alcoholic soln. of monomethylamine, or a 0·5 per cent. soln. of sodium hydroxide. When the process is repeated several times, the metal is almost completely peptized in distilled water. H. Schulze employed an analogous method of dispersion in 1885. The process was discussed by E. D. Desi, J. Pintsch, A. Pacz, F. J. Planchon, A. Lottermoser and W. Riedel, and E. W. von Siemens and J. G. Halske. A. Lottermoser discussed the colloidal content of tungsten powder. J. Billitzer obtained the colloidal metal by making an electric arc between tungsten electrodes under water. T. Svedberg prepared the **isobutylalcosol** by the electric dispersion method—**3**. 23, 10—and C. H. von Hoessle prepared hydrosols by electric dispersion. L. Hamburger studied the properties of thin films.

The term *single crystal*, or *unicrystal*, is applied to a wire or rod the whole of which is composed of one crystal. The term is not usually applied to the isolated crystals, say, when tungsten is deposited from its vapour. One-crystal wires were studied by G. Tammann,[7] J. Czochralsky, B. Duschnitz, I. Tarjan and P. Tary, Z. Jeffries, J. Pintsch, and H. C. H. Carpenter and C. F. Elam. Single crystals of tungsten wire were prepared in 1914 by J. Pintsch by drawing the ordinary squirted tungsten filament, containing a little thoria, through a zone raised to 2000° to 2200° in an atm. of hydrogen, and at a rate of about 3 metres per hour. The process was modified by F. S. Goucher, and R. Jacoby. The diameter of the single crystals of tungsten was increased by F. Koref, by glowing the wire in the vapour of tungsten hexachloride in the presence of hydrogen: $WCl_6=W+3Cl_2$, and $WCl_6+3H_2=W+6HCl$. The tungsten forms an adherent deposit on the wire, and as growth proceeds, the wire assumes a crystalline contour—four-, six-, or eight-sided—depending on the orientation of the crystal with respect to the axis of the wire. When the diameter of the wire has been increased 3 or 4 times, any further deposition results in the formation of new crystals with a different orientation. The microscope and the X-radiograms show that the structure of the deposit is identical with that of the original crystal. The subject was investigated by H. Fischvoigt and F. Koref, and by A. E. van Arkel. J. A. M. van Liempt also developed a method of increasing the diameter of single crystals by electro-deposition from acid lithium tungstate.

REFERENCES.

[1] W. Allen and A. Aiken, in A. and C. R. Aiken, *Dictionary of Chemistry*, London, **2**. 445, 1807; C. Hatchett, *Phil. Trans.*, **86**. 285, 1796; A. Ruprecht, *Ann. Chim. Phys.*, (1), **8**. 3, 1791; *Journ. Phys.*, **37**. 230, 1790; L. N. Vauquelin and L. Hecht, *Journ. Mines*, **4**. 19, 1796; J. J. Berzelius, *Schweigger's Journ.*, **16**. 476, 1816; *Ann. Phil.*, **3**. 245, 1814; *Ann. Chim. Phys.*, (2), **17**. 13, 1821; *Pogg. Ann.*, **4**. 147, 1825; **8**. 147, 267, 1826; C. F. Bucholz, *Schweigger's Journ.*, **3**. 1, 1811; F. Wöhler, *Pogg. Ann.*, **2**. 345, 1824; *Quart. Journ. Science*, **20**. 177, 1826; *Phil. Mag.*, **66**. 263, 1825; *Gött. Nachr.*, 35, 1850; *Liebig's Ann.*, **73**. 190, 1850; **77**. 262, 1851; *Ann. Chim. Phys.*, (2), **29**. 43, 1823; (3), **29**. 187, 1850; J. J. and F. de Elhuyar, *Análisis quimico del volfram y exámen de un nuovo metal que entra en su composicion*, Bascongada, 1783; *A Chemical Examination of Wolfram and Examination of a New Metal which enters into its Composition*,

London, 1785; *Chemische Zerkleiderung des Wolframs*, Halle, 1786; F. Jean, *Compt. Rend.*, **81.** 95, 1875; *Bull. Soc. Chim.*, (2), **25.** 65, 1876; *Ann. Chim. Anal. Appl.*, **9.** 321, 1875; G. A. Meerson, *Journ. Russ. Phys. Chem. Soc.*, **60.** 1217, 1928; F. A. Bernoulli, *Pogg. Ann.*, **111.** 573, 1860; *Chem. News*, **5.** 116, 1862; J. Waddell, *Amer. Chem. Journ.*, **8.** 280, 1886; *Chem. News*, **55.** 101, 112, 1887; *Trans. Roy. Soc. Edin.*, **33.** 1, 1889; *Zeit. phys. Chem.*, **3.** 491, 1889; A. Riche, *Ann. Chim. Phys.*, (3), **50.** 33, 1857; E. R. Schneider, *Pogg. Ann.*, **93.** 474, 1854; *Journ. prakt. Chem.*, (1), **50.** 154, 321, 1850; E. Zettnow, *Pogg. Ann.*, **130.** 16, 241, 1867; J. B. von Borck, *Journ. prakt. Chem.*, (1), **54.** 254, 1851; *Oefvers Akad. Förh.*, **8.** 147, 1851; R. F. Marchand, *Liebig's Ann.*, **77.** 263, 1851; H. Wright, *Liebig's Ann.*, **79.** 222, 1851; *Gött. Nachr.*, 181, 1851; K. Seubert and A. Schmidt, *ib.*, **267.** 218, 1890; L. Weiss and O. Aichel, *ib.*, **337.** 370, 1904; L. von Uslar, *ib.*, **94.** 255, 1855; *Beiträge zur Kenntniss des Wolframs und Molybdäns*, Göttingen, 1855; H. E. Roscoe, *Liebig's Ann.*, **162.** 359, 1872; *Proc. Manchester Lit. Phil. Soc.*, **11.** 79, 1872; *Chem. News*, **25.** 61, 73, 90, 1873; *Bull. Soc. Chim.*, (2), **25.** 61, 1873; W. Majert, *U.S. Pat. No.* 946551, 1909; E. Straub, *ib.*, 721638, 1903; E. Thomson, *ib.*, 960441, 1910; F. M. Becket, *ib.*, 854018, 1907; 930027, 930028, 1909; 1081569, 1910; C. M. Johnson, *ib.*, 964868, 964870, 964871, 1910; *Brit. Pat. No.* 25401, 1910; A. Stavenhagen, *Compt. Rend.*, **127.** 755, 1898; *Ber.* **32.** 1513, 3064, 1899; A. Stavenhagen and E. Schuchard, *ib.*, **35.** 909, 1902; J. Philipp, *Ber.*, **15.** 499, 1882; *Monit. Scient.*, (3), **20.** 74, 1878; C. W. Siemens and A. K. Huntington, *Chem. News*, **46.** 164, 1882; R. Saxon, *ib.*, **137.** 216, 1928; E. W. von Siemens and J. G. Halske, *German Pat., D.R.P.* 190233, 200886, 201283, 1906; H. Kuzel and E. Wedekind, *ib.*, 42377, 1909; Badische Anilin und Sodafabrik, *ib.*, 95694, 1911; P. Schwarzkopf, *ib.*, 39510, 1911; A. Sternberg and A. Deutsch, *ib.*, 69704, 1809; J. Schilling, *ib.*, 32750, 1909; *U.S. Pat. No.* 950869, 1909; *Zeit. angew. Chem.*, **24.** 910, 1911; H. Krieg, *ib.*, **6.** 50, 1893; *German Pat., D.R.P.* 66177, 1891; E. Ruhstrat, *ib.*, 215347, 1907; 217781, 1908; 220176, 1909; *Brit. Pat. No.* 24437, 1909; G. Arrivant, *Compt. Rend.*, **143.** 594, 1907; G. Chaudron, *Études des réactions réversibles de l'hydrogène et de l'oxyde de carbone sur les oxydes métalliques*, Paris, 1921; *Compt. Rend.*, **170.** 1056, 1920; S. M. Delépine, *ib.*, **131.** 184, 1900; *Bull. Soc. Chim.*, (3), **23.** 675, 1900; E. Defacqz, *Ann. Chim. Phys.*, (7), **22.** 239, 1901; H. Moissan, *ib.*, (7), **8.** 570, 1896; *Le four électrique*, Paris, 229, 1897; London, 159, 1904; *Compt. Rend.*, **73.** 13, 1872; **116.** 1225, 1893; **123.** 13, 1896; G. Gin, *ib.*, **125.** 213, 1897; *Oesterr. Zeit. Berg. Hütt.*, **55.** 81, 1907; J. L. F. Vogel, *Chem. Age*, **3.** 306, 1920; F. Filsinger, *Chem. Ind.*, **1.** 229, 1878; E. D. Clarke, *The Gas Blowpipe*, London, 79, 1819; H. N. Warren, *Chem. News*, **70.** 102, 1894; **75.** 2, 1897; D. J. Giles, *U.S. Pat. No.* 1348356, 1920; C. W. Davis, *Journ. Ind. Eng. Chem.*, **11.** 201, 1919; E. D. Desi, *Journ. Amer. Chem. Soc.*, **19.** 213, 1897; C. R. Schroeder, *U.S. Pat. No.* 1609970, 1926; J. W. Marden, *ib.*, 1646734, 1648954, 1927; H. Goldschmidt, *Zeit. Elektrochem.*, **4.** 494, 1898; H. Goldschmidt and C. Vautin, *Journ. Soc. Chem. Ind.*, **17.** 649, 1898; G. T. Holloway and H. W. Lake, *ib.*, **19.** 542, 1900; J. N. Pring and W. Fielding, *Journ. Chem. Soc.*, **95.** 1497, 1909; N. Parravano and C. Mazzetti, *Rec. Trav. Chim. Pays-Bas*, **42.** 821, 1923; Electrical Furnaces and Smelters, Ltd., *German Pat., D.R.P.* 247993, 1911; *French Pat. No.* 427537, 1911; O. Voigtländer, *ib.*, 455313, 1914; *German Pat., D.R.P.* 10743, 1913; J. C. Butterfield, *Brit. Pat. No.* 6936, 1909; 16562, 1915; C. J. Head, *ib.*, 155600, 1917; A. Pacz, *ib.*, 337160, 1929; A. S. Cachemaille, *ib.*, 238663, 239742, 1924; Philips Gloelampenfabriken, *ib.*, 200879, 1922; H. Lohmann, *ib.*, 157780, 1921; *Scient. Amer. Monthly*, **4.** 155, 1921; *Elektrochem. Zeit.*, **25.** 141, 1918; **26.** 29, 1919; A. E. van Arkel, *Chem. Weekbl.*, **24.** 90, 1927; A. Martin, *Ueber die Darstellung von metallischen Wolfram*, München, 42, 1908; N. Branoic, *Giorn. Bibl. Tech. Internat.*, **1.** 3, 1925; H. Kuzel and E. Wedekind, *Met. Chem. Engg.*, **12.** 260, 1914; L. Weiss and A. Martin, *Zeit. anorg. Chem.*, **65.** 302, 1910; V. I. Spitzin, *ib.*, **148.** 69, 1925; W. Prandtl and B. Bleyer, *ib.*, **64.** 223, 1909; J. A. M. van Liempt, *ib.*, **120.** 267, 1922; **122.** 175, 1922; **126.** 183, 226, 1923; **143.** 285, 1925; *Koll. Zeit.*, **32.** 118, 1923; *Zeit. Elektrochem.*, **31.** 249, 1925; B. Neumann, *ib.*, **14.** 169, 1908; L. Wöhler and O. Balz, *ib.*, **27.** 406, 1921; L. Wöhler and R. Günther, *ib.*, **29.** 276, 1923; L. Wöhler and W. Prager, *ib.*, **23.** 199, 1917; H. Alterthum and F. Koref, *ib.*, **31.** 508, 1925; F. Koref, *ib.*, **28.** 511, 1922; A. Burger, *Reduktion durch Calcium*, Basel, 17, 1907; K. Metzger, *Ueber Zirkon- und Wolframlegierungen*, München, 36, 1910; F. Kupelwieser, *Oesterr. Zeit. Beg. Hütt.*, **47.** 145, 1899; R. N. Riddle, *Amer. Journ. Science*, (3), **38.** 160, 1889; J. L. Gay Lussac and L. J. Thénard, *Recherches physicochimiques*, Paris, **1.** 517, 1811; E. A. G. Street, *Monit. Scient.*, (4), **9.** 623, 1895; G. A. Percival, *World Power*, **4.** 11, 1925; C. Reichard, *Chem. Ztg.*, **27.** 1, 1903; J. Férée, *Bull. Soc. Chim.*, (3), **19.** 128, 1898; G. Erhard, *Met.*, **9.** 441, 1912; D. Kremer, *Engg.*, **102.** 632, 1916; Anon., *ib.*, **104.** 432, 1917; *Eng. Min. Journ.*, **98.** 16, 1914; *Min. Scient. Press.*, **112.** 134, 1916; W. Baughman, *ib.*, **114.** 800, 1917; Anon., *Elektrochem. Zeit.*, **22.** 110, 146, 1915; G. Bessa, *L'Ind. Chim.*, **9.** 2, 1922; *Chem. Trade Journ.*, **70.** 199, 1922; L. R. Pratt, *Eng. Min. Journ.*, **90.** 959, 1910; M. R. Andrews and S. Dushman, *Journ. Franklin Inst.*, **192.** 545, 1921; W. C. Blake, *Journ. Western Soc. Eng.*, **27.** 223, 1922; C. H. Jones, *Chem. Met. Engg.*, **22.** 9, 1920; *Metal Ind.*, **16.** 107, 1920; W. Reinders and A. W. Vervloet, *Rec. Trav. Chim. Pays-Bas*, **42.** 625, 1923; L. and H. H. Kahlenberg, *Trans. Amer. Electrochem. Soc.*, **46.** 181, 1924; L. Kahlenberg and W. J. Trautmann, *ib.*, **39.** 377, 1921; O. L. Mills, *U.S. Pat. No.* 1721966, 1929; C. W. Blake, *Journ. Ind. Eng. Chem.*, **21.** 1002, 1929; H. W. Hutchin, *Trans. Cornish Inst. Eng.*, **5.** 28, 1917; *Iron Coal Traders Rev.*, **94.** 655, 1917; *Mining Mag.*, **17.** 39, 85, 1917; T. Sington, *Eng. Min. Journ.*, **109.** 879, 1920.

[2] E. F. Smith, *Ber.*, **13.** 753, 1880; *Amer. Chem. Journ.*, **1.** 329, 1880; J. A. M. van Liempt, *Canada Pat. No.* 284078, 1928; W. E. Koerner, *Trans. Amer. Electrochem. Soc.*, **31.** 211, 1917;

C. A. Mann and H. O. Halvorsen, *ib.*, **45**. 493, 1924 ; L. and H. H. Kahlenberg, *ib.*, **46**. 51, 181, 1924 ; O. Collenberg and K. Nilsson, *Zeit. Elektrochem.*, **31**. 555, 1925 ; O. Collenberg and J. Backer, *ib.*, **30**. 230, 1924 ; H. Leiser, *ib.*, **13**. 690, 1907 ; B. Neumann and H. Richter, *ib.*, **30**. 474, 1924 ; J. A. M. van Liempt, *ib.*, **31**. 249, 1925 ; *Zeit. anorg. Chem.*, **120**. 267, 1922 ; **122**. 175, 1922 ; **126**. 183, 1923 ; **143**. 285, 1925 ; F. M. Jäger and B. Kapma, *ib.*, **113**. 56, 1920 ; A. Fischer, *ib.*, **81**. 170, 1913 ; M. Junot, *L'Inst.*, 97, 1853 ; J. G. Children, *Phil. Trans.*, **99**. 32, 1809 ; **105**. 363, 1815 ; E. Zettnow, *Pogg. Ann.*, **130**. 5, 1867 ; L. A. Hallopeau, *Bull. Soc. Chim.*, (3), **19**, 997, 1898 ; (3), **21**. 266, 1899 ; *Compt. Rend.*, **127**. 755, 1899 ; *Ann. Chim. Phys.*, (7), **19**. 115, 1900 ; R. Wedekin, *German Pat., D.R.P.* 42377, 1909 ; H. Mennicke, *Die Metallurgie des Wolframs*, Berlin, 198, 1911 ; Wolframlampen A.G., *German Pat., D.R.P.* 231657, 237014, 1910 ; L. Weiss and A. Martin, *Zeit. anorg. Chem.*, **65**. 302, 1910 ; A. Martin, *Ueber die Darstellung von metallischen Wolfram*, München, 42, 1908 ; A. Rosenheim and R. F. Bernhardi-Grisson, *Ber. Internat. Cong. Appl. Chem.*, **7**. x, 120, 1911 ; R. F. Bernhardi-Grisson, *Die kathodische Reduktion der Wolframsäure*, Berlin, 1910 ; R. E. Pearson and E. N. Craig, *Canadian Pat. No.* 221041, 1922 ; E. W. von Siemens and J. G. Halske, *Brit. Pat. No.* 286457, 1927 ; L. St. C. Broughall, *ib.*, 320818, 1928 ; L. W. McCay and N. H. Furman, *Journ. Amer. Chem. Soc.*, **38**. 640, 1916 ; K. S. Jackson, A. S. Russell and J. L. Merrill, *Journ. Chem. Soc.*, 2394, 1929 ; J. Férée, *Bull. Soc. Chim.*, (3), **19**. 213, 1898 ; L. Andrieux, *Recherches sur l'électrolyse des oxydes métalliques dissoux dans l'anhydride borique ou dans les borates fondus*, Paris, 1929 ; *Ann. Chim. Phys.*, (10), **12**. 423, 1929 ; D. B. Keyes and S. Swann, *Bull. Eng. Univ. Illinois*, 206, 1930.

[3] A. J. Rossi, *Min. Ind.*, **11**. 693, 1902 ; R. M. Keeney and G. M. Lee, *West Chem. Met.*, **6**. 269, 323, 347, 1910 ; R. M. Keeney, *Trans. Amer. Electrochem. Soc.*, **24**. 127, 1913 ; *Carnegie Mem. Iron Steel Inst.*, **4**. 108, 1912 ; Zirkon Glühlampenwerke A.G., *German Pat., D.R.P.* 210326, 1906 ; J. J. Runner and M. L. Hartmann, *The Occurrence, Chemistry, Metallurgy, and Uses of Tungsten*, Rapid City, 1918 ; S. S. Steinberg, *Journ. Russ. Met. Soc.*, 1, 1926 ; G. Gin, *Oesterr. Zeit. Berg. Hütt.*, **55**. 81, 1907 ; *Trans. Amer. Electrochem. Soc.*, **13**. 481, 1908 ; Anon, *Eng. Min. Journ.*, **93**. 173, 1912 ; D. A. Lyon, R. M. Keeney and J. F. Cullen, *Bull. U.S. Bur. Mines*, 77, 1914 ; F. M. Becket, *U.S. Pat. No.* 854018, 1907 ; 930027, 930028, 1909 ; 1081569, 1910 ; A. Lederer, *Elect. World*, **55**. 819, 1910 ; *Brit. Pat. No.* 6936, 1909 ; Vereinigte Glühlampen A.G., *Austrian Pat. No.* 36726, 1909 ; *Electrotech. Maschinenbau*, **27**. 935, 1909 ; E. W. von Siemens and J. G. Halske, *German Pat., D.R.P.* 190233, 200886, 201283, 1906 ; F. M. Becket and W. C. Read, *U.S. Pat. No.* 1700655, 1929.

[4] H. Schulze, *Journ. prakt. Chem.*, (2), **32**. 399, 1885 ; C. Killing, *Journ. Gasbeleucht.*, **39**. 697, 1897 ; F. Uppenborn, *ib.*, **49**. 756, 1906 ; A. Voss, *ib.*, **50**. 1022, 1923 ; A. Zinck, *ib.*, **50**. 1023, 1907 ; O. Lummer, *ib.*, **56**. 687, 1912 ; G. Bredig, *Zeit. angew. Chem.*, **11**. 951, 1898 ; A. Müller, *Helios*, **19**. 504, 1913 ; *Zeit. angew. Chem.*, **27**. 545, 563, 1914 ; L. Hamburger, *ib.*, **28**. 291, 1915 ; C. R. Böhm, *Pharm. Ztg.*, **51**. 907, 921, 1906 ; *Chem. Ztg.*, **31**. 985, 1014, 1907 ; W. Böttger, *ib.*, **41**. 10, 1917 ; Wolframlampen A.G., *German Pat., D.R.P.* 182766, 1904 ; 184379, 1905 ; 185906, 193221, 1906 ; A. Just and F. Hanaman, *ib.*, 154262, 1903 ; *Electrochem. Met. Ind.*, **7**. 24, 1909 ; G. de Lamercodie, *Rev. Gen. Science*, **19**. 283, 1908 ; A. Blondel, *Bull. Soc. Internat. Elect.*, **82**. 79, 1908 ; A. Bainville, *L'Electricien*, (2), **36**. 236, 1908 ; M. G. Richard, *ib.*, (2), **38**. 46, 1909 ; C. Vallet, *ib.*, (2), **42**. 309, 1911 ; J. A. Montpellier, *ib.*, (2), **41**. 129, 1911 ; G. Laring, *Journ. Franklin Inst.*, **167**. 260, 1909 ; G. S. Merrill, *ib.*, **171**. 391, 1911 ; A. Salmony, *Chem. Ztg.*, **51**. 389, 1927 ; Anon., *Electrician*, **64**. 27, 1909 ; **66**. 623, 1910 ; **73**. 183, 1914 ; F. H. R. Lavender, *ib.*, **64**. 306, 1909 ; F. W. Wilcox, *ib.*, **68**. 935, 1910 ; K. Mey, *ib.*, **72**. 320, 1912 ; F. J. Brislee, *ib.*, **69**. 325, 1912 ; M. von Pirani and A. R. Meyer, *ib.*, **76**. 350, 1915 ; *Electrotech. Zeit.*, **36**. 498, 507, 1915 ; M. von Pirani, *Helios*, **18**. 46, 1912 ; B. Duschnitz, *ib.*, **20**. 601, 1914 ; *Elect. Rev. West. Elect.*, **56**. 32, 89, 1910 ; C. F. Fréry and C. Chéneveau, *Compt. Rend.*, **149**. 777, 1909 ; A. Berninger and R. Schuster, *Mitt. Tech. Gewerb.*, (2), **19**. 56, 1909 ; Anon., *Elect. World*, **56**. 144, 1910 ; W. H. Miller, *ib.*, **56**. 27, 1910 ; I. Langmuir and J. A. Orange, *ib.*, **62**. 798, 1912 ; *Met. Chem. Engg.*, **11**. 613, 1912 ; *Proc. Amer. Inst. Elect. Eng.*, **32**. 1895, 1912 ; J. W. Howell, *ib.*, **29**. 819, 1910 ; *Gen. Elect. Rev.*, **17**. 276, 1914 ; I. Langmuir, *ib.*, **19**. 208, 1916 ; *Phys. Rev.*, (2), **7**. 302, 1916 ; J. W. Howell, W. D. Coolidge and C. F. Scott, *Eng. News*, **64**. 7, 1910 ; F. Koref and K. Moers, *U.S. Pat. No.* 1635793, 1927 ; R. E. Meyer, *Trans. Amer. Inst. Chem. Engg.*, **3**. 172, 1910 ; A. Grau, *Oesterr. Chem. Ztg.*, **13**. 3, 1910 ; Anon., *Illuminating Eng.*, **4**. 23, 1911 ; *Monatsch. Elektrotech.*, **32**. 305, 1911 ; S. G. S. Dicker, *Brit. Pat. No.* 217322, 1923 ; H. Lohmann, *ib.*, 157769, 1921 ; J. F. Meyer, *Elect. Journ.*, **8**. 529, 1911 ; B. F. Fischer, *ib.*, **8**. 547, 1911 ; G. P. Scholl, *ib.*, **9**. 557, 1912 ; H. Schröder, *Gen. Elect. Rev.*, **14**. 426, 1911 ; Anon., *Tech. Moderne*, **8**. 193, 1914 ; *Elect. Rev.*, **74**. 595, 1914 ; A. B. Reeve, *Yale Science Mag.*, 1, 1912 ; O. H. Ogley, *Elect. Rev.*, **71**. 471, 1912 ; A. G. Oehler, *Wisconsin Eng.*, 3, 1911 ; R. Ziegenberg, *Zeit. Beleucht.*, **19**. 430, 445, 1912 ; C. Baskerville, *Trans. New York Elect. Soc.*, 1, 1912 ; A. R. Meyer, *Dingler's Journ.*, **328**. 305, 1913 ; A. Siemans, *Journ. Inst. Metals*, **9**. 42, 1913 ; *Engg.*, **95**. 365, 1913 ; A. Lederer, *Elect. Journ.*, **10**. 1166, 1913 ; E. J. Dailey, *ib.*, **13**. 251, 1915 ; G. M. J. MacKay, *Trans. Illuminating Eng. Soc.*, **9**. 775, 1914 ; R. F. Glazebrook and C. C. Patterson, *Researches Nat. Phys. Lab.*, **10**. 159, 1914 ; E. A. Gimingham and S. R. Mullard, *Journ. Inst. Elect. Eng.*, **54**. 15, 1915 ; C. Eisler, *Machinery*, **23**. 321, 1916 ; R. W. Hutchinson, *High Efficiency Electrical Illumination*, New York, 1911 ; G. B. Barham, *The Development of the Incandescent Lamp*, London, 1912 ; J. G. Escard, *Les lampes électriques*, Paris, 1912 ; C. Mourlon, *La nouvelle industrie des lampes électriques à filaments métalliques*, Bruxelles, 1911 ; C. H. Weber, *Die elektrischen Metallfadenglühlampen*, Leipzig, 1914 ; N. L. Müller, *Zeit. angew. Chem.*, **26**.

404, 422, 1912; *Fabrikation und Eigenschaften der Metalldrahtlampen*, Halle a. S., 1914; R. Jacoby and F. Koref, *U.S. Pat. No.* 1739234, 1929; C. A. Hansen, *Brass World*, **9**. 401, 1913; C. H. Jones, *Chem. Met. Engg.*, **22**. 9, 1920.

[5] W. D. Coolidge, *Trans. Amer. Inst. Elect. Eng.*, **29**. 961, 1910; *Elect. World*, **56**. 1368, 1910; *Eng. News*, **64**. 7, 1910; O. Ruff, *Zeit. angew. Chem.*, **25**. 1889, 1912; N. L. Müller, *ib.*, **26**. 404, 422, 1912; *Fabrikation und Eigenschaften der Metalldrahtlampen*, Halle, a.S., 1914; British Thomson-Houston Co., *Brit. Pat. No.* 11409, 1906; 25557, 1908; 5821, 1909; W. Geiss and J. A. M. van Liempt, *Zeit. anorg. Chem.*, **168**. 107, 1927; Anon., *La Tech. Moderne*, **6**. 193, 1914; *Elect. Rev.*, **74**. 595, 1914; C. J. Smithells, *Tungsten*, London, 42, 1926; Westinghausen Metallfaden-Glühlampenfabrik, *Austrian Pat. No.*, 41247, 1906; Z. Jeffries, *Trans. Amer. Inst. Min. Eng.*, **56**. 571, 1916; F. A. Fahrenwald, *ib.*, **54**. 541, 1916; *Journ. Nat. Dental Assoc.*, **4**. 372, 1917; C. G. Fink, *Trans. Amer. Elektrochem. Soc.*, **17**. 229, 1910; **22**. 499, 1912; *Met. Chem. Engg.*, **8**. 341, 1910; *Elect. World.*, **55**. 1185, 1910; Anon., *ib.*, **57**. 627, 1911; *Elektrotech. Maschinenbau*, **36**. 477, 1915; *Electrician*, **76**. 633, 1916; R. W. Moore, *Met. Chem. Engg.*, **12**. 186, 1914; O. Kruh, *Elektrotech. Maschinenbau*, **31**. 313, 338, 1913; A. Lederer, *Elect. Journ.*, **10**. 1175, 1913; P. Schwarzkopf and S. Burgstaller, *U.S. Pat. No.* 1096464, 1914; F. Koref and H. Alterthum, *ib.*, 1650631, 1927.

[6] J. Férée, *Bull. Soc. Chim.*, (3), **19**. 128, 1898; C. R. Böhm, *Zeit. Beleucht.*, **19**. 491, 1912; *Chem. Ztg.*, **37**. 1431, 1913; H. Kuzel, *ib.*, **37**. 1431, 1913; *Zeit. Beleucht.*, **19**. 492, 1912; *German Pat., D.R.P.* 30900, 186980, 194348, 197379, 1905; 199962, 1907; 208599, 1908; *Austrian Pat. No.* 2572, 2573, 1906; L. Hamburger, *Koll. Zeit.*, **23**. 177, 1918; A. Lottermoser, *Koll. Zeit.*, **36**. 53, 1922; T. Svedberg, *Die Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe*, Dresden, 488, 1920; *Ber.*, **39**. 1713, 1906; H. Schulze, *Journ. prakt. Chem.*, (2), **32**. 399, 1885; J. Pintsch, *German Pat., D.R.P.* 205581, 206911, 1905; 216785, 1906; A. Pacz, *ib.*, 245190, 1909; 249733, 1910; F. J. Planchon, *ib.*, 220981, 220982, 1908; E. W. von Siemens and J. G. Halske, *ib.*, 194468, 1906; 200939, 201462, 1907; J. Billitzer, *Zeit. angew. Chem.*, **11**. 951, 1898; E. D. Desi, *Journ. Amer. Chem. Soc.*, **19**. 239, 1897; C. H. von Hoessle, *U.S. Pat. No.* 1491250, 1924; A. Lottermoser and W. Riedel, *Koll. Zeit.*, **52**. 133, 1930.

[7] G. Tammann, *Lehrbuch der Metallographie*, Leipzig, 15, 1914; H. C. H. Carpenter and C. F. Elam, *Journ. Inst. Metals*, **24**. 83, 1920; J. Pintsch, *German Pat., D.R.P.* 291994, 1914; R. Gross and N. Blassmann, *Neues Jahrb. Min. B.B.*, **42**. 728, 1919; R. Gross, *Jahrb. Rad. Elektron.*, **15**. 270, 1918; R. Jacoby, *U.S. Pat. No.* 154899, 1925; E. Sutter, *Die Entstehung von Eisenkristallen und ihre Wachstumsbedingungen mit Berücksichtigung der Vorgänge bei der allotropen Umwandlung*, Griefswald, 1926; J. A. M. van Liempt, *Zeit. Elektrochem.*, **31**. 249, 1925; I. Tarjan and P. Tary, *Chem. Rund. Miteleuropa*, **4**. 165, 1927; A. E. van Arkel, *Physica*, **3**. 76, 1923; H. Fischvoigt and F. Koref, *Zeit. tech. Phys.*, **6**. 298, 1925; F. Koref, *Zeit. Elektrochem.*, **28**. 511, 1922; J. Czochralsky, *Zeit. phys. Chem.*, **92**. 219, 1918; B. Duschnitz, *Helios*, **32**. 361, 1926; Z. Jeffries, *Journ. Inst. Metals*, **20**. 109, 1918; F. S. Goucher, *Phil. Mag.*, (6), **48**. 229, 1924; (7), **2**. 289, 1926; *Brit. Pat. No.* 181703, 1920.

§ 5. The Physical Properties of Tungsten

The **colour** of the metal prepared by J. J. and F. de Elhuyar,[1] by the carbon reduction process, is steel-grey, with a strong metallic lustre. If slowly reduced at a high temp. the powder is coarse-grained, and grey, but if reduced slowly at a low temp., it is fine-grained and black (F. Wöhler, J. J. Berzelius, H. E. Roscoe, and M. E. Pennington and E. F. Smith). C. W. Siemens and A. K. Huntington said that the metal which has been fused is white and brittle, with a very close grain. The metal as prepared by F. Wöhler, by hydrogen reduction, is a silver-grey or tin-white powder. H. von Wartenberg said that the purified metal has the colour of highly polished platinum; and L. Weiss added that it has a colour resembling that of mercury. C. J. Smithells and H. P. Rooksby observed that the microstructure of a sample of tungsten showed small grains with sub-boundaries having a nearly uniform orientation in each crystal; these sub-boundaries are formed under the influence of stresses formed during the rapid cooling of the metal. E. Zettnow said that the powder consists of tabular **crystals** which are probably tetragonal prisms, but, as was shown by P. Debye, the crystals are cubic. This is proved by the interference figures and the **X-radiograms.** The space-lattice is a body centred cube, Fig. 3; the length of the edge of the cube is

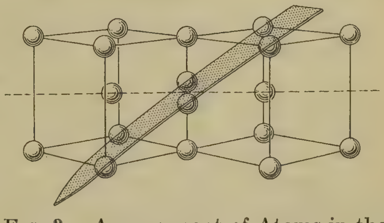


Fig. 3.—Arrangement of Atoms in the Tungsten Crystal, and the (112)-plane.

$a=3{\cdot}18\times10^{-8}$ cm.; A. W. Hull gave 3·272 A.; and W. P. Davey gave $a=3{\cdot}155$ A. The distance of closest approach of the atoms is $2{\cdot}732\times10^{-8}$ cm.; and if the at. wt. is 184, the calculated density is 19·32, which approaches the highest observed values. A. E. van Arkel, F. Skaupy, K. Becker, E. Schmid, T. Fujiwara, H. C. Burger, W. Herme-Rothery, J. Leonhardt, W. Rosenhain, J. Hengstenberg, and R. Gross and N. Blassmann studied this subject. F. S. Goucher found that between ordinary temp, and the m.p., no change occurs in the space-lattice except that due to thermal expansion; so that there is no evidence of an allotropic form of tungsten. The powder, spluttered films, and worked tungsten have all the same lattice structure —*vide infra*, tensile strength. A. E. van Arkel, F. S. Goucher, J. Hengstenberg and H. Mark, W. G. Burgers, H. C. Burger, and E. Schiebold discussed the deformation of the lattice by mechanical action—*vide infra*—and W. Braunbek, by raising the temp. J. A. M. van Liempt, and F. Koref and H. Wolff observed no measurable difference respectively in the heats of combustion, and from the heats of dissolution of worked and unworked tungsten. W. Geis and J. A. M. van Liempt calculated an increased energy content of 775 cals. per gram-atom of tungsten by cold working of the metal. They observed no evidence of a compression of the space-lattice by compression or rolling, and concluded that the phenomenon is physical and has to do with electrons; it is not a question of structure or of crystallography. G. Tammann and M. Straumanis, T. Fujiwara, and M. Ettisch and co-workers discussed the structure of hard-drawn tungsten wires. The **cleavage** is about the (100)-plane, but the slip planes on deformation are the (112)-planes—Fig. 3. E. Sutter obtained over-growths with iron. A polished section of wire or rod does not show the crystalline structure, but inclusions like thoria are visible. J. Leonhardt studied the crystal's structure. The metal is most rapidly attacked by etching reagents on the (112)-plane, and the **corrosion figures,** as shown by B. Schmidt, R. Gross and N. Blassmann, and C. J. Smithells, differ from those obtained with metals like iron, which, although having the same lattice structure, etch most readily on the (100)-planes, and show cubic etch-pits. The grain structure readily appears when the polished surface is etched for $\frac{1}{2}$ to 10 minutes with boiling 3 per cent. hydrogen dioxide; with a cold soln. of equal vols. of 10 per cent. sodium hydroxide and 30 per cent. potassium ferrocyanide; or with a hot soln. of hydrofluoric and nitric acids and water (3 : 1 : 4). Electrolysis etching is more difficult to control. R. Gross and co-workers found that when a hollow tungsten cylinder, in which the direction of the crystallographic axis was constant throughout, was etched with an alkaline soln. of potassium ferrocyanide, six equal faces were developed on the interior, and six on the exterior of the cylinder. The interior faces were set at 30° to the adjacent exterior faces. This relative position is in accordance with the rule that the exterior faces developed on an etched cylinder are the planes of maximum soln. velocity, those on the interior the planes of minimum velocity.

When the temp. of a pressed ingot of tungsten is raised by the passage of an electric current, no change in **grain-size** occurs below 1000°–1050°; above that temp., the average grain-size increases, and the sp. gr. of the ingot increases, until, for a given temp., equilibrium is attained, and no appreciable change in structure takes place. The equilibrium grain-size is larger the higher the temp., and equilibrium is apparently reached in about 15 minutes. According to H. Alterthum, true equilibrium should not be attained until the ingot consists of one crystal; and if the period of heating be sufficiently prolonged at temp. a little below the m.p., this state is nearly attained. The time required to form the nuclei of crystals decreases rapidly as the temp. is raised. Thus, at 3000°, the time required for the formation of nuclei is 180 min.; at 3100°, 110 min.; and at 3200°, 45 min. S. Ohashi found the relation between the temp., $\theta°$, of crystallization and the time, t, of heating for the recrystallization of single crystal wires of tungsten is $\theta=1250-250\log t$. Z. Jeffries and R. S. Archer gave 1200° for the lowest temp. of recrystallization. According to G. A. Meierson, the growth of crystals of tungsten does not commence below 1200° if the powdered metal be heated in a stream of dry hydrogen. Should the latter contain moisture, growth commences at 1050°, and is accompanied by loss in weight of the sample. These effects are due to the formation of tungsten dioxide, which is volatile at 1050°. This, on being reduced, deposits tungsten on the crystals. Similarly, the formation of large crystals of tungsten in the reduction of tungstic anhydride is due to the volatility of the oxides WO_3 and W_2O_5, which assumes measurable proportions at 850° and 900°, respectively. Where tungsten is prepared by the reduction of the trioxide the magnitude of the crystals of the latter has no influence on that of the product. Similarly, it is possible to prepare large crystals of dioxide by slow reduction of trioxide at an appropriate temp.

The ingot is not uniformly heated by the electric current. Z. Jeffries, and C. J. Smithells have shown that there may be a difference of 150° between the centre and the surface, and between the middle portion and the ends fitted with water-cooled contacts. The largest crystals are produced at the lowest temp. capable of producing exaggerated growth; the average grain-size of the metal decreases as the temp. rises. Hence, also, since the rate of growth increases rapidly with temp., larger grains are formed in the centre of the ingot than in the outer layers; and the large grains absorb their smaller neighbours. Exaggerated growth occurs from about 2500° to 2800°; below this range of temp., the ingot remains fine-grained—Fig. 4; and above, grain growth occurs throughout the metal without any marked contrast developing. Z. Jeffries found that this effect is exaggerated when there is any obstruction to the growth of the grains. For example, the presence of, say, 0·75 per cent. of thoria, increases the differences in the grain-size by restraining the growth of the small grains, while the large grains grow around and include the obstruction. F. Sauerwald observed that the growth of the grains of loose tungsten powder under its own weight occurs at about 2500°, the exact temp. depends upon the size of the grains, and on the magnitude of the press. Thus, grain-growth can be detected at 950° with powder of 0·6μ average diameter, and with 3μ diameter grain-growth occurs 70° higher. With a 0·6μ powder, grain-growth occurs at 1200° with a press. of 10 tons per sq. in.; at 1050°, with a press. 2½ times as great; and at 900°, with a press. 4 times as great. The cause of the growth of the grains is attributed to a reduction in the surface energy when the grain-size increases; the finer the particles, the more readily do the grains grow, and this is favoured by the greater the number of contacts with fine grains than with coarse ones. Z. Jeffries and R. S. Archer gave 1200° for the recrystallizing temp. of tungsten. The subject was studied by J. A. M. van Liempt. M. Ettisch and co-workers found that the crystallites in soft wires are irregularly arranged, and in hard wires regularly. The subject was discussed by C. J. Smithells and co-workers, F. Sauerwald, W. G. Burgers, and H. P. and W. P. Davey. T. Fujiwara found that when the crystals of tungsten are deposited by the action of steam on polycrystalline and unicrystalline tungsten rods heated in moist hydrogen, the crystals formed on polycrystalline rods were rhombic dodecahedra with the (110)-faces sometimes appearing as hexagonal prisms, and some of the crystals were laminated. In the case of unicrystalline rods, the crystals on the etched surface had the same orientation as the parent crystal to which they were united by a (110)-plane.

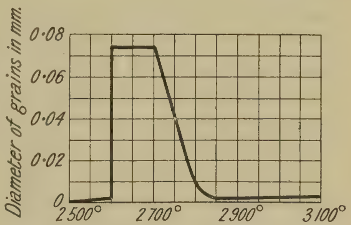


Fig. 4.—The Effect of Temperature on the Grain-size of Tungsten.

The early determinations of the **specific gravity** of tungsten were too low, no doubt owing to the impurity of the metal. For instance, J. J. and F. de Elhuyar[2] gave 17·6; C. F. Bucholz, 17·4; W. Allen and A. Aiken, 17·22; F. A. Bernoulli, 17·1 to 18·2; E. Zettnow, 17·20 to 18·4 at 17·5°; L. von Uslar, 16·54 to 18·26 at 21°; A. Riche, 17·2; and H. E. Roscoe, 19·129 at 17°/4°. Among the more recent determinations, G. Arrivant gave 15·8; J. Waddell, 18·5; L. A. Hallopeau, 18·68 at 0°; H. Moissan, 18·7; M. E. Pennington and E. F. Smith, 18·64 at 0°; E. F. Smith and F. F. Exner, 19·0; A. Stavenhagen, 16·6; S. M. Delepine, 18·61 to 18·67; L. Weiss, 18·72 at 20°; H. von Wartenberg gave 17·6 to 18·3 for massive tungsten, and 19·0 to 19·2 for the powder. F. Koref found the sp. gr. of unannealed tungsten to be 19·19; and after heating to 1050°, 19·23; 1225°, 19·23; 1525°, 19·26; 1900°, 19·26; 2200°, 19·26; and 2500°, 19·26. C. G. Fink found the value 18·81 before drawing into wire, and 19·30, 19·58, and 19·86 when drawn into wire respectively 150, 10, and 1·5 mils in diameter. W. Geiss and J. A. M. van Liempt observed that the cold working of tungsten leads to 19·35 for the density. This is in agreement with the value computed from the X-radiogram. This means that there is no evidence of a compression of the space-lattice by hammering or rolling. P. Hidnert and W. T. Sweeney gave 19·211 for 99·98 per cent. tungsten. From the X-radiograms, H. C. Burger obtained 19·37 when that of sodium chloride is 2·164. According to J. W. Avery and C. J. Smithells, there are changes in the sp. gr. of wires produced by the effects of the lubricant on the surface during the drawing of the wire; by the oxidation of fine wires; and by surface tension effects when small masses are weighed in liquids. The surface impurities must be removed before the sp. gr. of the metal is determined; and the extent of the attack on the underlying metal affects the sp. gr. Thus, a wire of 0·05 mm. diameter and sp. gr. 18·50, had a sp. gr. of 18·51 after it had lost 0·1 per cent. by etching with a soln. of sodium dioxide; 18·92 after a loss of 3·87 per cent.; and 18·91 after a loss of 14·50 per cent. With coarser wires, the change in the sp. gr. is smaller. This means that the wires have an outer layer of smaller sp. gr. than the mass of the wire, and representing a larger proportion of the whole wire, the more its diameter is reduced. The sp. gr. of a tungsten ingot increases rapidly as its diameter is reduced by rolling, etc., so that after a 75 per cent. reduction in sectional area, the sp. gr. is 19·23—the value deduced from the X-ray spectral data is 19·32. This initial increase is due to the closing of the pores in the metal; a subsequent decrease in the sp. gr. is connected with the break up of the crystal grains. The results with 99·998 per cent. tungsten, *A*, and tungsten with 0·75 per cent. thoria, *B*, with wires of diameter *d* mm., are as follows:

d	56	5·0	3·0	1·0	0·3	0·05	0·03
A	17·0	18·45	19·20	19·23	19·22	19·20	18·95
B	17·25	18·70	19·09	19·10	19·00	18·97	18·82

M. L. Huggins estimated the **atomic radius** of tungsten to be 1·58 A.; L. Vegard gave 1·04 A. Observations were made by V. M. Goldschmidt, L. Pauling, and E. T. Wherry from which it follows that the value for sexivalent tungsten is 0·88 A., for quadrivalent tungsten 0·66 to 0·68 A.; and for typical tungsten atoms, 1·37 A. H. G. Grimm, J. C. Slater, and A. M. Berkenheim studied the at. radius; and P. Vinassa, the mol. number. H. Schröder, and E. Donath and J. Mayrhofer discussed the atomic volume; and I. Traube, the at. soln. vol. L. von Uslar said that the **hardness** of tungsten is greater than that of agate; and H. Moissan added that when free from carbon it does not mark glass; and it may be filed with ease. C. G. Fink gave 4·5 to 8·0 for the hardness on Moh's scale; J. R. Rydberg, 9·0; and L. Wiss, 6·5 to 7·5. A. G. Worthing and W. E. Forsythe gave for the hardness respectively on Rockwell's and the sclerescopic scales: One-inch ingot, 20, and 45; the same ingot when swaged to 0·75 in. gave for the surface: 39, and 55·5, and for the centre: 23, and 35; and swaged tungsten gave 45, and 83—for compression, the values for tool-steel are respectively 61 and 95, showing that tungsten is only slightly less hard than tool-steel. E. W. Engel gave 290 for Brinell's hardness; and said that the metal can be filed and ground, but not easily machined. According to F. Koref, fine tungsten wires consisting of a single crystal may be softened by tempering for a short time above 2100° without recrystallization taking place, provided that the amount of deformation which the metal has undergone does not exceed a certain critical limit depending on the nature of the drawing and the thickness of the wire. Thick wires readily recrystallize after only slight reduction in area, whereas thin wires may be reduced 80 per cent. before recrystallization sets in on tempering. All metallic single crystals appear to be strained internally during growth, and unless this strain is removed by suitable tempering the metal works badly and readily recrystallizes on subsequent annealing. The density of the wires increases during tempering and the electrical resistance also changes. E. Ruhstrat found that if tungsten be heated in the electric arc, and abruptly quenched, it becomes so brittle that it can be ground to a fine powder.

H. Moissan observed that tungsten can be welded like iron by hammering at a temp. below its m.p.—*vide supra*, ductile tungsten. Z. Jeffries found a progressive increase in the **tensile strength** of an ingot of tungsten as it is swaged and drawn into wire. Taking the diameter in mils (a mil is 0·001 inch) and the tensile strength in lbs. per sq. in., he found for an ingot 200 mils × 250 mils, 18,000; for swaged rod, 216 mils diam., 50,600; 125 mils, 107,000; 80 mils, 176,600; and 26 mils, 215,000; and for drawn wire, 18 mils, 264,000; 7·23 mils, 340,000; 578 mils, 366,000; 5·50 mils, 378,000; 3·96 mils, 483,000; and 1·4 mils, 590,000. The tensile strength of the drawn wire between 3 and 20 mils is an exponential function of the diameter, and increases more slowly with the finer sizes. F. S. Goucher found also that with a single crystal loaded in tension, the time required for fracture to take place is an exponential function of the load and temp. C. J. Smithells added that the hardness can be reduced by annealing, but it cannot be removed without exceeding the temp. of recrystallization. Coupled with great strength, drawn tungsten wire is markedly ductile at ordinary temp. C. G. Fink gave for the tensile strength of tungsten wires 5·0, 2·8, 1·5 and 1·2 mils in diam., the respective values 460,000, 480,000, 550,000, and 580,000 lbs. per sq. in. J. Königsberger gave 270 to 285 kgrms. per sq. mm. for the tensile strength of tungsten wires; and 100 to 120 kgrms. per sq. mm. for single crystal wires. R. Tajime found the tensile strength of tungsten wire containing one per cent. of thorium, and having a diameter of 0·076 mm., is, in vacuo:

	27°	523°	1323°	1723°	2123°	2523°	2883°
Tensity .	310	200	70	20	9	4·5	1·5 kgrms. per sq. cm.

F. von Göler and G. Sachs gave the results in Fig. 5 for the tensile strength in kgrms. per sq. mm. of 0·1 mm. wires which have been heated to different temp.

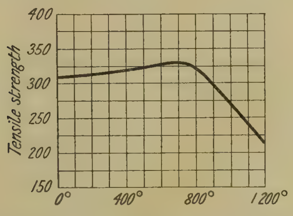


Fig. 5.—The Tensile Strength of Tungsten Wires heated to different temperatures.

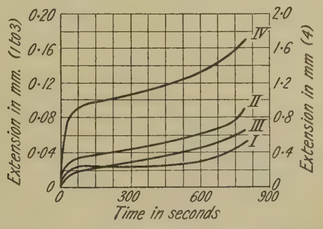


Fig. 6.—The Elongation of Single Crystals of Tungsten under Constant Load.

S. J. Wright gave $3{\cdot}886 \times 10^{12}$ dynes per sq. cm. for Young's modulus. C. H. Jones gave values for wires ranging up to 427 kgrms. per sq. mm.

F. S. Goucher showed that with single crystal wires extended under a constant load, there is first a rapid extension which hardens the metal, and thereafter, the extension continues at a uniform rate until the wire breaks. There is no change in the orientation of the crystal when it is in the most favourable position for slip and the sectional area is decreasing, hence it follows that the resistance to slip is proportional to the applied stress—Curves I to III, Fig. 6. With a multicrystal wire, the observed effect is the joint effect of all the crystals in which slip occurs, so that the extension—time curve has the same form—Curve IV, Fig. 6. With an aggregate of fine crystals the same relation may not be true because the rate of hardening may be modified by the crystal boundaries. When the diameter of single crystal wires is reduced by drawing through dies, they rapidly lose their characteristic ductility, becoming hard and eventually brittle; at the same time there is an increase in the tensile strength which is at first rapid. Thus, F. Koref found for the one-crystal wire prepared by J. Pintsch's process:

Diameter .	0·160	0·149	0·142	0·125	0·070 mm.
Tensity .	105·5	135	137	149	178 kgrms. per sq. mm.

The hardness may be removed by heating the wire to a high enough temp., so that the one per cent. elongation of the hardened wire increases 8 per cent. on annealing. Thus, for a single crystal wire 0·07 mm. diam., the tensile strength was 119 kgrms. per sq. mm.; when drawn to 0·052 mm., 133; when annealed 10 min. at 1500°, 130; 10 min. at 1800°, 130; 0·5 min. at 2100°, 130; and 10 min. at 2100°, 119. According to F. Koref, recrystallization occurs on heating if the reduction in area exceeds 60 to 80 per cent.; the temp. at which this occurs is lower the greater the amount of deformation, and it may occur at a temp. below that required for the removal of the hardness. Single crystal wires can therefore be reduced in area by alternately drawing and annealing to remove hardness provided the reduction in area at each stage does not exceed a critical value. F. Koref discussed the effect of crystal structure on the mechanical properties of tungsten; E. C. Bain and Z. Jeffries, the effect of mechanical work on the crystalline structure; and H. B. de Vore and W. P. Davey, the preferred orientation caused by mechanical work. F. S. Goucher measured the rate of flow of tungsten single crystals under constant load at 1000° K. and 2000° K. The results show an internal hardening which increases rapidly in the early stages of deformation and which tends to become proportional to the increase of stress in the later stages; this stage occupies the major portion of the time required for the fracture of such crystals. The hardening is greater at the lower temperature, and there is evidence that the rate of deformation is an important factor in the hardening process. This hardening may be removed by annealing at 2500° K. for 2 min. An X-ray study of these crystals at all stages of their deformation reveals distortions—crystallographic in nature—which increase progressively with the degree of deformation. Annealing these crystals produces no apparent alteration of this distortion.

Z. Jeffries and R. S. Archer found the effect of temp. on the tensile strength of two kinds of tungsten wire (No. 1—cold drawn; No. 2—annealed—Fig. 7), and observed that the tensile strength increases on a falling temp. but is lower at —185° than at room temp. This effect has been observed only with tungsten. The effect of temp. on the reduction in area, Fig. 8, increases with rising temp. The reduction in area is greater with the cold drawn than with the annealed wire. The effect of temp. on the elongation increases on a falling temp., Fig. 9, until

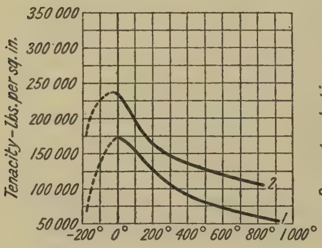


FIG. 7.—The Effect of Temperature on the Tensile Strength.

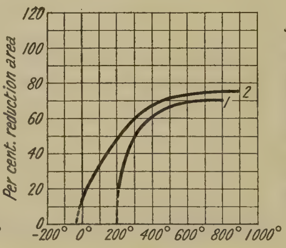


FIG. 8.—The Effect of Temperature on the Reduction in Area.

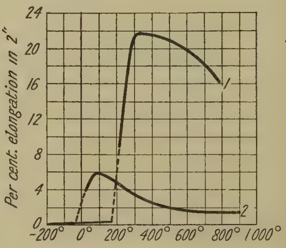


FIG. 9.—The Effect of Temperature on the Elongation.

the region of low temp. brittleness is attained. The maximum elongation occurs at lower temp. the greater the amount of cold working, but the actual elongation at this maximum decreases as the amount of working increases. Comparing the elongation and tensile strength curves, it follows that the development of brittleness is accompanied by a sharp rise in the tensile strength. F. S. Goucher also found that the tensile strength of drawn wire is greatest at about 0° but falls off rapidly at about 727°, probably owing to recrystallization. Long crystals produced by annealing at about 2727° have a lower tensile strength at 0°; and a single crystal wire, containing 2 per cent. of thoria, has a tensile strength about 3 times that of tungsten alone. The load in kgrms. per sq. mm. required to fracture a single crystal wire in one minute at different temp. is illustrated by Fig. 10. Most of the fractures below 527° are intercrystalline, showing that the crystal is stronger than the crystal boundaries. There are sharp changes in the curves near 577°, 1327°, and 2377°; these are said to be consistent with the electrical resistance curve of I. Langmuir; and with the thermal expansion curve of A. G. Worthing. The meaning of the discontinuities is unknown. W. E. W. Millington and F. C. Thompson also studied the plastic deformation of wires of single crystals of tungsten. P. Hidnert and W. T. Sweeney added that the "transformation points appear to be erroneous, and inconsistent with the work of other investigators."

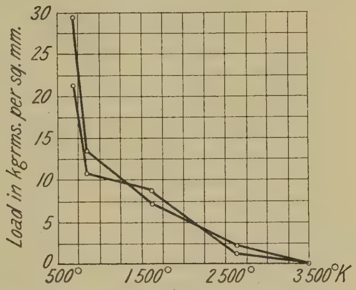


Fig. 10.—The Tensile Strength and Temperature Curve of Single Crystal Wires.

E. Grüneisen said that tungsten has the highest known **elastic limit** with the possible exception of iridium. S. J. Wright gave for Young's modulus $E = 3{\cdot}886 \times 10^{12}$ dynes per sq. cm., taken longitudinally. W. Geiss found the modulus of elasticity E can be represented as a function of the temp., T° K. for single crystal wires by $E=E_0\{(T_m-T)T_m^{-1}\}^{0\cdot263}$, where T_m denotes the m.p. on the absolute scale, and E_0 the modulus at 27°, or 40,000 kgrms. per sq. mm. H. Schönborn found the elasticity of drawn wire is in accord with Hooke's law, and varies from 34,800 to 37,300 kgrms. per sq. mm. at room temp., and falls to 3200 kgrms. per sq. mm. at 1027°. H. L. Dodge studied the effect of temp. on the elasticity of tungsten. He gave $35{\cdot}5+10^{11}$ dynes per sq. cm. at 20°, a value rather lower than C. G. Fink's $41{\cdot}4 \times 10^{11}$ dynes per sq. cm. The modulus was found to decrease uniformly with a rise of temp. up to 1000°, at which temp. it is $32{\cdot}3 \times 10^{11}$ dynes per sq. cm. A. L. Kimball and D. E. Lovell gave $38{\cdot}7 \times 10^{11}$ dynes per sq. cm. for the elastic modulus of swaged tungsten; and W. Widder, $E=E_{20}\{1 \times 0{\cdot}0003472(\theta-20)\}$. The **torsion modulus** of tungsten was found by W. Schriever to be greater than that of any other known material, the value at 2527° being equal to that for steel at room temp. W. Geiss gave for the torsion modulus G, as a function of the temp., T° K., $G=G_0\{(T_m-T)T_m^{-1}\}^{0\cdot263}$, where T_m denotes the m.p. on the absolute scale, and G_0, the modulus at 0°, or 17,100 kgrms. per sq. mm. at 27°. L. P. Sieg found large variations with different samples of tungsten. According to W. Schriever, the torsion varies from 9000 to 22,000 kgrms. per sq. mm. at room temp. and decrease slightly with temp. up to 727°; between 727° and 1727° the modulus falls more rapidly, being 3060 kgrms. per sq. mm. at 1727°. The value for equiaxial tungsten is greater than for drawn wire, and increases with grain-size. Both the torsion modulus and the tensile strength increase as the diameter of the wire decreases. J. Konigsberger gave $8{\cdot}1 \times 10^{11}$ to $9{\cdot}1 \times 10^{11}$ C.G.S. units for the torsion modulus of tungsten wires, and $15{\cdot}5 \times 10^{11}$ to 18×10^{11} C.G.S. units for single crystal wires. E. Edwards and co-workers examined the increase in the torsional stiffness produced by increasing the tension of tungsten wires. S. J. Wright gave $1{\cdot}514 \times 10^{12}$ dynes per sq. cm. for the **modulus of rigidity** of tungsten.

T. W. Richards and E. P. Bartlett found the **compressibility** of tungsten to be $2\cdot85\times10^{-7}$ at 20°, and it appears to be smaller than that of any known metal. P. W. Bridgman found the vol. compressibility of single crystal wires to be: $-\delta v/v=2\cdot18\times10^{-7}p-1\cdot4\times10^{-12}p^2$ at 30°; and $-\delta v/v=3\cdot18\times10^{-7}p-1\cdot5\times10^{-12}p^2$ at 75°; for swaged rod, $-\delta v/v=2\cdot93\times10^{-7}p-1\cdot5\times10^{-12}p^2$ at 30°; and $-\delta v/v=2\cdot95\times10^{-7}p-1\cdot5\times10^{-12}p^2$ at 75°; and for drawn wire, $-\delta v/v=3\cdot15\times10^{-7}p-1\cdot6\times10^{-12}p^2$ at 30°; and $-\delta v/v=3\cdot16\times10^{-7}p-1\cdot5\times10^{-12}p^2$ at 75°. The compressibility β, at 30° for drawn wire and swaged rod are, respectively, $\beta=0\cdot0_6315$ and $0\cdot0_6293$; $\delta\beta/\beta\delta p=0\cdot0_4102$ and $0\cdot0_4102$; $-\delta\alpha/\alpha\delta p=0\cdot0_52$ and $0\cdot0_54$; and $-\beta^{-1}(\delta\alpha/\alpha\delta p)=1\cdot24$ and $13\cdot7$, where α denotes the coeff. of thermal expansion. L. H. Adams gave $\delta\beta=-0\cdot03$. T. W. Richards gave for the **internal pressure,** 13,400 megabar at 20°; R. F. Mehl gave 1020 kilomegabars, and for the maximum disruptive press., 3570 kgrms. per sq. mm. K. Iokibe and S. Sakai gave for the **viscosity** of tungsten, at 16°, $\eta=9\cdot37\times10^8$; and G. Subrahmaniam, $8\cdot638\times10^8$. A. L. Kimball and D. E. Lovell also made observations on the internal friction of tungsten. P. W. Bridgman studied the effect of pressure on the rigidity. For the **diffusion** of carbon, and of thorium in tungsten, *vide infra;* G. Grube and K. Schneider, and J. Laissus studied the diffusion of tungsten into iron; and J. M. Eglin, of barium into tungsten.

C. G. Fink[3] found the coeff. of **thermal expansion** of a tungsten wire, 0·005 in. diam., to be $\alpha=0\cdot0_5336$ between 20° and 100°; and he gave $\alpha=0\cdot0_543$ for tungsten. I. Langmuir gave $0\cdot0_538$ between 1000° and 1500°; $0\cdot0_544$ between 1500° and 2000°; and $0\cdot0_541$ between 1000° and 2000°. H. L. Dodge obtained $0\cdot0_5456$ over the range 20° to 675°. If l be the length of the filament at 300° K., then, for a temp., T° K., between 1200° K. and 2500° K., $\delta l/l=0\cdot00245(T-300)\times10^{-3}+0\cdot000567(T-300)^2\times10^{-6}$. A. G. Worthing obtained $0\cdot0_5444$ at 27°; $0\cdot0_556$ between 1000° and 1500°; $0\cdot0_566$ between 1500° and 2000°; $0\cdot0_561$ between 1000° and 2000°; or $0\cdot0_5519$ at 1027°; and $0\cdot0_5726$ at 2027°. If l_0 is the length at 300° K., and l the length at a temp. T° K. between 1200° K. and 2700° K., $\delta l/l_0=0\cdot0_5449(T-300)+0\cdot0_{12}24(T-300)^3$; and for temp. T° K. between 300° K. and 2700° K., $\delta l/l_0=0\cdot0_5444(T-300)+0\cdot0_{10}45(T-300)^2+0\cdot0_{12}22(T-300)^3$; or

T° K. . .	330°	1200°	1500°	1800°	2100°	2400°
α . . .	$0\cdot0_5444$	$0\cdot0_5506$	$0\cdot0_5550$	$0\cdot0_5606$	$0\cdot0_5674$	$0\cdot0_5754$

The results of A. G. Worthing can be represented by $l=l_{27}(1+0\cdot0_5444\theta+0\cdot0_{10}45\theta^2+0\cdot0_{12}220\theta^3)$, and D. W. Berlin's results were in agreement with this. W. Widder gave 0·00000456 at 20°, and 0·0000038 at −190°. K. Becker gave $0\cdot0_575$ between 18° and 2200°; $0\cdot0_566$ between 18° and 1750°; and $0\cdot0_558$ between 18° and 1380°. J. Disch gave:

	−190° to 0°	−100° to 0°	0° to 100°	0° to 200°	0° to 300°	0° to 400°
α . . .	$0\cdot0_538$	$0\cdot0_541$	$0\cdot0_545$	$0\cdot0_546$	$0\cdot0_547$	$0\cdot0_548$

or, if l_0 refers to the length at 0° and l the length at θ°, $l=l_0(1+0\cdot0_5446\theta+0\cdot0_973\theta^2)$ between 0° and 400°; and $l=l_0(1+0\cdot0_5445\theta+0\cdot0_8328\theta^2)$ between −190° and 200°. F. S. Goucher said that there is evidence of discontinuities in the thermal expansion at about 850° K., 1600° K., and 2650° K., but P. Hidnert and W. T. Sweeney and others have not been able to confirm this statement. P. Hidnert and W. T. Sweeney represented their results between −105° and 502° by $l=l_0(0\cdot0_5428\theta+0\cdot0_958\theta^2)$; and they found the average values to increase regularly with temp.:

	−100° to −50°	−50° to 0°	0° to 50°	50° to 100°	100° to 200°	200° to 300°	300° to 400°
α . . .	$0\cdot0_542$	$0\cdot0_543$	$0\cdot0_543$	$0\cdot0_544$	$0\cdot0_545$	$0\cdot0_546$	$0\cdot0_547$

	400° to 500°	−100° to 0°	0° to 100°	0° to 200°	0° to 300°	0° to 400°	0° to 500°
α . . .	$0\cdot0_548$	$0\cdot0_542$	$0\cdot0_543$	$0\cdot0_544$	$0\cdot0_545$	$0\cdot0_545$	$0\cdot0_546$

and for the range −100° to 500°, $\alpha=0\cdot0_545$. W. D. Coolidge gave 0·35 cal. per cm. per degree for the **thermal conductivity** of tungsten; S. Weber, 0·383 cal.

per cm. per degree or 1·605 watts per cm. per degree at 0°, and T. Barratt and R. M. Winter, 0·476 cal. per cm. per degree at 17°, and 0·472 cal. at 100°. The relation of the thermal and electrical conductivities was studied by E. Grüneisen and E. Goens. A. G. Worthing found that the thermal conductivity in watts per cm. per degree increases linearly from 1000° K. to about 2500° K.:

T° K. . .	1000°	1300°	1600°	1900°	2200°	2500°	2800°
Conductivity	0·84	0·93	1·02	1·09	1·15	1·21	1·27

C. Zwikker gave for the thermal conductivity, k watts per cm. per degree:

T° K. . .	1800°	2000°	2200°	2400°	2600°	2800°
k . . .	1·22	1·29	1·33	1·37	1·405	1·43

H. V. Regnault[4] found the **specific heat** of tungsten to be 0·03342; and L. Weiss, 0·0358. J. Dewar gave 0·0095 between —253° and —196°; P. Nordmeyer and A. L. Bernoulli, 0·0357 between —185° and 20°; A. W. Grodspeed and E. F. Smith, 0·0338 between 20° and 100°; H. Mache, 0·0336 between 0° and 100°; E. Defacqz and M. Guichard, 0·0340 between 15° and 93°; and 0·0375 between 15° and 423°; M. von Pirani, 0·033 at 340°; 0·036 at 1000°; and 0·041 at 1350°; W. Geiss and J. A. M. van Liempt gave 0·0323; O. M. Corbino, 0·0334; whilst K. K. Smith and L. I. Bockstahler gave 0·045 between 2375° K. and 2475° K.—this is eq. to an at. ht. of 8·3. K. K. Smith and P. W. Bigler found 0·0479 for the sp. ht. at 2095° to 2212°. The last-named results were discussed by P. F. Gaehr. H. A. Jones and co-workers gave $C_p=4\cdot70+0\cdot0015T$. W. Geiss and J. A. M van Liempt observed no perceptible difference in the sp. ht. of cold-drawn and of crystallized metal. The corresponding **atomic heat** varies from 1·75 between —253° to —196° to 8·75 between 2095° and 2212°. F. Wüst and co-workers gave $C_p=6\cdot17$ at 100°, and 6·72 at 1500°. F. Lange found for the sp. ht. 0·47 at —240°; 1·00 at —230°; 1·65 at —220°; 2·26 at —210°; 2·78 at —200°; 3·25 at —190°; and 3·69 at —180°; and W. M. Latimer obtained 6·0 for the at. ht., C_p, between 250° and 900°. F. M. Jäger and E. Rosenbohm gave for temp. up to 1300°, and for tungsten free from oxide, $c_p=0\cdot02744+0\cdot132672\times10^{-4}\theta-0\cdot091488\times10^{-8}\theta^2+0\cdot067812\times10^{-11}\theta^3$, or abbreviated, $c_p=0\cdot0274412+0\cdot0000132\theta$. H. Danz gave:

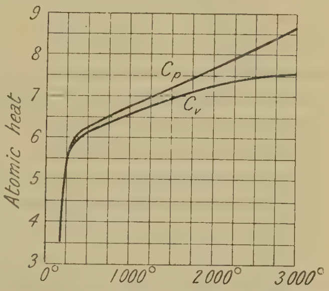


Fig. 11.—The Effect of Temperature on the Atomic Heats of Tungsten.

	400°	500°	600°	700°	800°	900°
C_p . . .	7·199	7·304	7·409	7·515	7·620	7·724
C_v . . .	7·092	7·180	7·264	7·347	7·429	7·506

C. Zwikker gave the following results, Fig. 11, for the at. ht. of tungsten at different temp. on the absolute scale:

°K. . .	100°	200°	300°	600°	900°	1200°
C_p . . .	3·77	5·32	5·90	6·23	6·57	6·90
C_v . . .	3·77	5·30	5·87	6·15	6·44	6·71
°K. . .	1500°	1800°	2100°	2400°	2700°	3000°
C_p . . .	7·23	7·56	7·89	8·22	8·56	8·89
C_v . . .	6·96	7·18	7·36	7·50	7·62	7·70

F. M. Jäger and E. Rosenbohm made analogous observations. A. Magnus and H. Danz gave for the at. ht. of 99 per cent. tungsten over the range 400° to 900°, $C_p=6\cdot7807+0\cdot0010475\theta$; and A. Magnus and H. Holzmann, $C_p=5\cdot8947+0\cdot0_383338\theta$ between 100° and 900°; and H. A. Jones and I. Langmuir gave $C_p=4\cdot7+0\cdot0015T$ for the at. ht. between 900° and the m.p.; C_p is here expressed in cals. per gram-atom per degree. Since the vol. of a wire 1 cm. long and 1 cm. diamter is $\frac{1}{4}\pi$ c.c., the conversion factor from cals. per gram-atom to watt seconds per degree is $\pi \times 19{\cdot}35 \times 4{\cdot}185/4 \times 184 = 0{\cdot}3456$. He discussed the application of P. Debye's formula. A. G. Worthing obtained for the at. ht., 6·20 at 330° K.; 6·50 at 1200° K.; 6·95 at 1500° K.; 7·40 at 1800° K.; 7·85 at 2100° K.; and 8·30 at 2400° K.; and for the at. ht. at constant vol. he gave 5·95 at ordinary temp., 6·25 at 1200° K., and 7·35 at 2400° K. A. G. Worthing also found that E. Grüneisen's relation a/C_p rises from $7{\cdot}16 \times 10^{-7}$ at 330° K. to $9{\cdot}08 \times 10^{-7}$ at 2400° K. E. D. Eastman and co-workers computed $C_p - C_v = 0{\cdot}050$ Cal. per degree per mol. A. Magnus and H. Holzmann, O. M. Corbino, L. I. Bockstahler, and H. Hunkel also obtained values in close agreement with those of A. G. Worthing. J. Maydel discussed some relations of the sp. ht.; and W. M. Latimer, the thermal energy of the electrons in tungsten.

According to C. W. Siemens and A. K. Huntington,[5] tungsten can be fused in the electric arc furnace; H. Moissan also fused the metal in the arc furnace, and noted that it is less fusible than chromium and molybdenum. L. Weiss fused the metal by heating it in the electric arc, between graphite electrodes; and the Allgemeine Electrizitäts Gesellschaft obtained fused tungsten from rods made of the compressed powder as anodes for the electric arc. There are difficulties in determining the m.p. of the highly purified metal with a disappearing filament pyrometer: (i) The fixing of the thermometer scale; and (ii) when the pyrometer is focussed on the surface of the molten metal the observed "brightness" temp. has to be corrected for the spectral emmissivity. If a block of fused tungsten be under black body conditions, *i.e.* contained in an enclosed vessel whose walls are uniformly heated to a temp. T, its temp. will be T; if the block of tungsten could be removed without altering its temp., and its brightness matched with the disappearing filament pyrometer, its temp. would appear to be at some lower temp. say, T_b, called the *brightness temperature.* If instead of matching the brightness of the tungsten, its colour be matched against that of the black body, it will appear to have another temp., say, T_c, called the *colour temperature* with tungsten, the colour temp. is always higher than the true temp. by about 0·6 per cent. at 1000° K., and 2·3 per cent. at 3500° K. The brightness temp. is related to the true temp. by the equation $T^{-1} - T_b^{-1} = C_2^{-1}\lambda 2{\cdot}303 \log_e e\lambda$, where $e\lambda$ is the spectral emissivity for a wave-length λ, and C_2 is a constant. If the temp. of the block of tungsten be measured by comparing the rate of radiation of energy with that of the black body, its temp., say T_r, is called the *radiation temperature,* will be lower than the true temp. This subject was discussed by C. Zwikker, R. Davis and K. S. Gibson, E. Lax and M. Pirani, F. Wolfers, H. A. Jones, F. Henning and W. Heuse, M. L. Phillips, H. Hunkel, and H. C. von Alphen. C. Zwikker gave $T^{-1} - T^{b-1} = \lambda C_2^{-1} 2{\cdot}303 \log_e e\lambda$, where $C_2 = 14{,}330\mu$ degree. A. G. Worthing and W. E. Forsythe found for the corresponding temp., up to the m.p. (3655° K.):

True temp., T .	1000°	1500°	2000°	2500°	3000°	3500°	3655° K.
Colour temp., T_c .	1006°	1517°	2033°	2557°	3094°	3646°	3817° K.
Brightness temp., T_b	966°	1420°	1857°	2274°	2673°	3053°	3165° K.
Radiation temp., T_r	581°	991°	1428°	1859°	2286°	2704°	— °K.

H. von Wartenberg gave 2800° to 2850° for the **melting point** of tungsten; M. von Pirani, 3100°, and 3250°; O. Ruff and O. Goecke, 2575° for 99·2 per cent. tungsten, and O. Ruff gave 2650° for the pure metal. C. W. Waidner and G. K. Burgess said that the m.p. is 3080°; W. E. Forsythe, 3027°; W. R. Mott, 3402°; M. von Pirani and A. R. Meyer gave 3100°; I. Langmuir, 3267°; and G. P. Luckey, and A. G. Worthing, 3357°—and 3372° to 3392°—M. von Pirani and H. Alterthum obtained 3387° for the m.p. of tungsten melting under black body conditions; and F. Henning and W. Heuse similarly obtained 3370°. G. P. Luckey found that the effect of the pressure of the atmosphere of nitrogen on the m.p. is represented by 3350° at 1 atm. press.; 3321° at 8 atm.; 3309° at 14 atm.; 3289° at 21 atm.; and 3291° at 28 atm. P. Woog discussed the hollow-ing out of tungsten bars by central fusion by the passage of a heavy electric current; and L. P. Sieg, the relation between the m.p. and the coeff. of elasticity.

C. W. Siemens and A. K. Huntington, and H. Moissan noted the volatilization of tungsten when it is melted in the electric arc furnace. E. Tiede and E. Birnbräuer found that in a vacuum furnace tungsten at 2450° yields a sublimate of rhombic or rhombohedral crystals—as indicated above, the crystals are cubic. When the sublimate condenses in a crystalline form on hot surfaces, a mirror is formed on a cold surface. M. Arndt observed that when an electric arc with a tungsten anode is heated in vacuo, the vaporized metal condenses in films. M. R. Mott gave 6300° for the **boiling point**; I. Langmuir calculated 4727°; and C. G. Fink, 3700°. According to I. Langmuir, the **rate of evaporation** of tungsten in vacuo, m grms. per sq. cm. per second, at T° K., is $\log m=15\cdot402-47444T^{-1}-1\cdot4\log T$:

T° K.	1600°	2000°	2400°	2800°	3200°	3655°
m .	$3\cdot7\times10^{-20}$	$2\cdot32\times10^{-14}$	$1\cdot58\times10^{-10}$	$8\cdot28\times10^{-8}$	$8\cdot79\times10^{-6}$	$4\cdot70\times10^{-4}$

The subject was discussed by H. A. Jones and co-workers, and M. R. Andrews. C. Zwikker gave $\log M=11\cdot92-4\cdot84\times10^4T^{-1}-0\cdot368\log T-0\cdot00016T$, where M denotes the number of grams evaporated per sq. cm. per second, and

T° K. .	1500°	2000°	2500°	3000°	3400°
M .	$0\cdot0_{21}178$	$0\cdot0_{13}155$	$0\cdot0_{9}833$	$0\cdot0_{5}105$	$0\cdot0_{4}708$

G. R. Fonda found that the rate of evaporation is independent of the diameter of the wire between 0·051 and 0·254 mm.; but it is affected by the grain-size. Thus, for a fine-grained wire at 2900° K., M has a mean value of 4×10^{-7}, but with a coarse-grained wire, $M=2\cdot6\times10^{-7}$. The rate of evaporation determines the limit of temp. at which the filament lamp can be operated. I. Langmuir showed that the rate of evaporation is reduced if the filament is surrounded by an atmosphere of a neutral gas. G. R. Fonda found that with a wire 0·051 mm. in diameter, the rates of evaporation in vacuo and in nitrogen were respectively $M=420$ and 21; and with a 0·69 mm. wire in nitrogen and in argon $M=13$, and 9 respectively. W. H. Rodebush observed the value of A in the equation for the number of electrons, n, evaporating from a metal filament per sq. cm. per sec., $n=AT^{-\frac{1}{2}}e^{-b/T}$, to be $1\cdot48\times10^{26}$ when the calculated result at 2000° K. is $6\cdot00\times10^{26}$. The subject was studied by S. Weber, F. J. Wilkins, E. Oosterhuis, and G. R. Fonda. The last-named observed that the rate of evaporation of tungsten filaments at 2870° K. in a mixture of argon with 14 per cent. nitrogen varies from 2×10^{-9} to 230×10^{-9} grm. per sq. cm. per sec. as the pressure is reduced from 1650 to 0 mm. A. G. Worthing and W. C. Baker observed that the rate of evaporation of tungsten is positively affected by strong electrostatic fields, the effect disappears if the field strength is less than a million volts per cm. H. Alterthum studied the effect of salt vapours on the evaporation of tungsten. The volatility of tungsten is increased in a vacuum lamp if the metal has been sprayed with various salts—particularly the halogen salts. Reaction occurs between the filament and the wall as well as on the filament and at the wall. I. Langmuir found that the **vapour pressure** of tungsten, p mm., can be represented by $\log p=15\cdot502-47444T^{-1}-0\cdot9\log T$, for

T° K.	2000°	2400°	3200°	3400°	3540°	5100°
p .	$6\cdot5\times10^{-12}$	$4\cdot92\times10^{-8}$	$4\cdot67\times10^{-5}$	$3\cdot20\times10^{-4}$	0·08	760

The values at the m.p., 3540° K., and the b.p., 5110° K., have been obtained by extrapolation. P. Winternitz also calculated values for the vap. press. of tungsten: $\log p=-48982\cdot72T^{-1}+1\cdot78\log T+3$, so that $p=1$ at 5100°; and J. A. M. van Liempt gave $\log p=-46440T^{-1}+9\cdot15$. W. Herz said that the **heat of fusion** has a value between 1000 and 5000 cals.; and I. Langmuir, that the latent **heat of vaporization** at a temp. T° K. is $\lambda=218,000-1\cdot8T$ cals. per gram-atom. This is greater than the heat developed by any known chemical reaction. P. Winternitz gave 223,900 cals. per gram-atom at room temp.; M. R. Andrews, 177,000 cals.;

and F. S. Mortimer, 201,200 cals. L. Hamburger and co-workers discussed the trouble attending the use of tungsten filaments by the sublimation of the metal on to the walls of the glass bulbs. J. A. M. van Liempt gave 40·49 to 41·62 for **Trouton's constant**; and I. Langmuir, 3·5 for the **chemical constant**—F. Simom gave 0·012. M. Delépine and L. A. Hallopeau gave for the **heat of oxidation,** (W,3O)=195·41 Cals. at constant vol., and 196·3 Cals. at constant press.; and (W,2O)=131·4 at constant press. L. Weiss gave 321·08 Cals. per eq. for the heat of combustion. J. E. Moose and S. W. Parr gave 1059 cals. per gram, or 194·9 Cals. per mol.; W. G. Mixter, 196·3 Cals. per mol. J. A. M. van Liempt observed that the difference between the heats of oxidation per gram atom of worked and unworked tungsten, *viz.* 193·5 and 195·0 Cals. is within the limits of experimental error; and F. Koref and H. Wolff found the heats of dissolution of cold-drawn, and recrystallized tungsten show no measurable difference. G. N. Lewis and co-workers, and E. D. Eastman gave 8·4 for the at. **entropy** of tungsten at 25°; R. C. Tolman, 53·7 at 25°; B. Bruzs gave 8·4 at 25°, and 27·4 at the m.p.; and W. Herz, 14·60. The subject was discussed by W. M. Latimer, W. Herz, and by E. D. Eastman and co-workers. R. D. Kleeman discussed the internal and free energy of tungsten.

H. von Wartenberg[6] found the **index of refraction** of tungsten to be $\mu=2{\cdot}76$; the **absorption coefficient,** $k=2{\cdot}71$; and the **reflecting power,** $R=48{\cdot}6$ per cent., for $\lambda=0{\cdot}579\mu$. A. G. Worthing found μ and k for tungsten at 27° to be respectively 3·86 and 0·81, and at 1627°, respectively 3·85 and 0·89. W. W. Coblentz found for the percentage reflecting power, R, of tungsten for light of wave-length λ:

λ	0·4	0·5	1·0	2·0	4·0	6·0	8·0	10·0	12·0
R	47·0	49·3	62·3	84·6	92·8	94·6	95·6	95·5	96·3 per cent.

J. T. Littleton found at room-temp., $R=54{\cdot}5$ per cent. when $\lambda=0{\cdot}589\mu$. The subject was discussed by G. Jaffé. F. E. Dix and L. H. Rowse gave for the indices of refraction, μ, extinction coeff., μk, and percentage reflecting power, R:

λ	670	630	570	490	450	370	350
μ	1·52	1·42	1·28	1·11	1·08	0·87	0·82
μk	3·65	3·60	3·27	2·94	3·38	2·78	2·57
R	70·9	70·2	67·8	66·0	69·1	69·0	67·1

W. Weniger and A. H. Pfund studied the reflecting power of tungsten; and R. Hamer examined the effect in the ultra-violet. A. Grau studied the luminosity curves of tungsten. A. G. Worthing measured the **spectral emissivity,** e, by heating tungsten tubes drilled with small holes, and measuring the ratio of the brightness of holes (under black body conditions) to the brightness of the outer tungsten surface. He found for temp. up to the m.p. 3655° K.:

	T° K.	300°	1000°	1500°	2000°	2500°	3000°	3500°	m.p.
e	0·665μ	0·470	0·456	0·445	0·435	0·425	0·415	0·405	0·402
	0·467μ	0·505	0·486	0·476	0·469	0·462	0·455	0·449	0·447
	mean	—	0·464	0·457	0·452	0·446	0·440	0·434	0·433
	colour	—	0·396	0·383	0·370	0·355	0·343	0·329	0·324
	total	0·032	0·114	0·192	0·260	0·303	0·334	0·351	0·304

B. T. Barnes studied the emissivity of carbonized tungsten. E. P. Hyde and co-workers represented the relation between the colour temp., T_c, and the total radiation, $I_r=aT_c^{4\cdot93}$, where a is a constant. C. Zwikker gave for the spectral emissivity, $e\lambda$, for $\lambda=0{\cdot}665\mu$, and the total radiation, I_r, in watts per sq. cm.,

T° K.	1200°	1500°	2000°	2500°	3000°	3400°
$e\lambda$	0·458	0·451	0·440	0·427	0·415	0·407
I_r	1·70	5·52	24·0	69·4	162	291

H. A. Jones gave for the radiation, I_r, from the surface in watts per sq. cm.,

T° K.	273°	300°	500°	1000°	1500°	2000°	2500°	3000°	3655°
I_r	0	0·0416	0·00970	0·602	5·54	23·9	69·2	160·1	399·4

C. Zwikker found that if B is the brightness of a black body at T_c, expressed in international candles per sq. cm., and B_0 the brightness of tungsten at T_b, $B=B_0e^{C_2/2\cdot3303\lambda(T_b^{-1}-T_c^{-1})}$. The subject was discussed by G. Holst and co-workers. The total emissivity, e_T, is given by the relation $I_r=e_T\sigma T^4$, where I_r represents the radiation intensity, *i.e.* the total radiation per unit area, and σ is a constant. The normal brightness, B, at any temp. is the candle power per sq. cm. measured in a direction normal to the surface :

T° K. .	1000°	1500°	2000°	2500°	3000°	3500°	m.p.
B .	0·00012	0·33	20·0	237·5	1257	4220	5740

Tungsten deviates from the cosine law for luminous radiation which requires that an element of the light source shall appear equally bright from any angle Actually, as the angle varies from normal to grazing incidence, the brightness increases and decreases rapidly. The efficiency of the light emissivity of a tungsten filament is measured by the ratio of the input in watts to the light emitted expressed in terms of lumens per watt. Let I_r denote the total radiation intensity in watts per sq. cm. ; and E, the luminous efficiency in lumens per watt :

T° .	300°	1000°	1500°	2000°	2500°	3000°	3500°	3655°
I_r .	0·0015	0·654	5·55	23·72	67·60	153·9	300	360
E .	—	—	0·20	2·78	11·67	27·1	45·9	53·1

E. O. Hulbert measured the variations in the emissivity of tungsten wires for light of wave-length from λ=3200 A. to 5500 A. between 1746° K. and 2785° K., and found :

λ .	3478	3956	4435	4916	5400	5641 A.
E .	0·470	0·484	0·466	0·460	0·447	0·436

Observations were also made by F. Henning, and E. Furthmann. M. Luckiesh and F. K. Moss discussed the luminosity of the tungsten lamp. The eye is not equally sensitive to light of all wave-lengths ; according to B. P. Dudding and C. J. Smithells, there is a maximum in the relative visibility for light of wave-length $0{\cdot}0_455$ cm. The luminous value of the radiation renders it necessary to multiply the energy at each wave-length by the relative visibility. The efficiency, E, increases as the temp. is raised, but at the same time there is a slight decrease owing to the radiation becoming selective, and approaching that of a black body. A. G. Worthing and W. E. Forsythe found for a tungsten wire 1 cm. long and 1 cm. diameter, in vacuo, the following value for the current, C amps., the fall of potential, V volts, the resistance, R ohms, the power, P watts, and the luminous flux, in lumens :

T° K. . .	300°	1000°	1500°	2000°	2500°	3000°	3500°	3655°
R . . .	$0{\cdot}0_5718$	32·73	53·35	75·20	98·40	122·5	147·2	155
V . .	$0{\cdot}0_457$	8·23	30·7	75·5	146·3	247·7	381	428
C . .	$0{\cdot}0_58$	0·251	0·575	1·004	1·487	2·020	2·59	2·76
P . . .	0·00045	2·068	17·62	75·8	217·5	501·0	985	1180
Lumens .	—	0·0012	3·3	208·5	2490	13300	45200	61800

B. E. Shackelford discussed the difference in the brightness of the inner and outer surfaces of a heated tungsten helical filament ; G. Ribaud, the relation between the current and the temp. of tungsten filaments ; and W. Geiss, the relation between the total radiation and the electric resistance. The efficiency of a tungsten filament in vacuo determines its temp., and this enables the temp. scale to be reproduced. R. E. Nyswander measured the selective radiation in the ultra-red and found a maximum for $\lambda=2{\cdot}3\mu$ at 1278° ; for $1{\cdot}9\mu$ at 1547° ; for $1{\cdot}7\mu$ at 1729° ; for $1{\cdot}61\mu$ at 1826° ; for $1{\cdot}52\mu$ at 1934° ; for $1{\cdot}475\mu$ at 1994° ; and for $1{\cdot}425\mu$ at 2063°. The bands of selective emission in the ultra-red observed by R. E. Nyswander were shown by W. W. Coblentz to be atm. absorption bands. The wave-length of the maximum emission of a tungsten filament lamp was $1{\cdot}43\mu$, and with a carbon filament lamp, $1{\cdot}48\mu$. A. H. Taylor discussed the luminous efficiency of tungsten filament lamps ; H. B. Dorgelo, the absorption of light by tungsten ; A. G. Worthing the deviations of the light from the cosine law ; W. E. Forsythe and F. Christison, A. L. Hellgott, and B. T. Barnes, the energy of the radiation ; and H. C. von Alphen, the radiation.

The **emission of electrons** from hot tungsten has been studied by O. W. Richardson,[7] H. Jones and R. Whiddington, N. A. de Bruyne, T. E. Stern and co-workers, H. L. van Velzer and W. R. Ham, E. H. Hall, A. H. Warner, L. P. Smith, W. E. Forsythe and E. M. Watson, R. A. Millikan and C. C. Lauritsen, F. Rother and E. Münder, P. A. Ross, R. J. Piersol, R. S. Bartlett, I. Langmuir, A. C. Davies and R. N. Moss, W. R. Ham and M. W. White, K. K. Smith, H. E. Krefft, W. Hüttemann, L. H. Germer, E. Lorenz, A. T. Waterman, J. M. Eglin, L. A. du Bridge, J. A. Becker and D. W. Mueller, H. Klumb, C. C. Lauritsen and S. S. Mackeown, L. I. Bockstahler, C. del Rosario, S. C. Roy, H. E. Farnsworth, H. E. Ives, H. Hunkel, F. E. Colpitts, H. Nukiyama and H. Horikawa, W. B. Nottingham, C. E. Berger, E. Meyer, E. Spiller, W. H. Brattain, G. P. Thomson, K. Sixtus, H. N. Kozangwsky, C. C. van Voorhis and K. T. Compton, and S. Dushman and co-workers—*vide* tantalum, **9.** 65, 2. According to H. H. Lester, the work, ϕ, done by an electron in escaping from the surface of tungsten is 4·478 eq. volts ; and, according to R. Hamer, the longest wave-length of radiation which can cause photoelectric emission of electrons is 2615 A. S. Dushman and co-workers found for the electronic current, $i=60{\cdot}2T^2e^{-52600/T}$; and the relations between the emission in ampères per sq. cm. and temp. calculated from this equation for well-aged tungsten filaments as well as for thoriated tungsten, are :

$T°$ K.		800°	1500°	2000°	2500°	2800°
Electron emission	tungsten	—	$7{\cdot}58\times10^{-8}$	$8{\cdot}92\times10^{-4}$	0·267	3·12
	Th-tungsten	$1{\cdot}20\times10^{-11}$	$1{\cdot}82\times10^{-2}$	9·55	117·5(2300°)	—

C. Zwikker made observations on this subject ; he found for the thermionic emission, $i=60{\cdot}2T^2e^{-52230/T}$ amp. per sq. cm., or

$T°$ K.	1500°	2000°	2500°	3000°	3400°
i	$0{\cdot}0_6102$	0·00112	0·302	14·9	149

I. Langmuir found that higher values for electron emission are obtained from filaments containing 1 to 2 per cent. thoria. With an ordinary thoriated filament, the thorium is present as the dioxide, and the electronic emission is the same as for tungsten alone ; but if the temp. is raised above 2600° K., the thoria reacts with the tungsten to form thorium. This reaction was studied by C. J. Smithells. I. Langmuir found that the thoriated filament heated to 2600° K. gives the normal value for tungsten at 1500° K. since the thorium metal will have evaporated from the surface. It is therefore necessary after flashing the thoriated filament at 2800° K. for, say, 3 min. to lower the temp. to about 2000° K. to allow the thorium to diffuse to the surface from the interior. The emission at 1500° K. is then 100,000 times the value for tungsten alone—*vide supra.* If the temp. is kept below 1900° K., this high value is retained indefinitely, but it is destroyed above 2200° K. owing to the volatilization of the thorium. According to A. S. Cachemaille, and the British Thomson-Houston Co., the presence of reducing agents like carbon, or boron, or tungsten carbide favours the reduction of the thoria to thorium. W. G. Burgers, and J. A. M. van Liempt discussed this subject. I. Langmuir and K. H. Kingdon found that the thorium surface is destroyed by bombardment with positive ions. The lowest voltage, V, at which spluttering occurs in different gases ; and the ratio, n, of the thorium atoms removed to the number of impacting ions at 150 volts, are :

	H	Ne	Ar	Cs	Hg	He
V	600	45	47	52	55	(35)
n	0	0·023	0·080	0·084	0·044	0·00015

I. Langmuir and co-workers, and J. A. Becker also found that if the tungsten filament be heated to 1200° in the sat. vapour of cæsium, the cæsium is attracted by the tungsten surface, and provided the temp. is below 1200° K., the metals evaporate so slowly that the surface becomes covered with a layer of cæsium ions, and the electron emission is greatly augmented. If the filament has a layer of adsorbed ions, the cæsium ions are retained more firmly. According to S. Kalandyk, iodine decreases the positive emission of a new tungsten filament, but does not affect one previously heated. It also increases the negative emission from tungsten. W. H. Crew found that light augments the emission of electrons from hot filaments. R. H. Fowler discussed the electron theory of thermionic emission; C. C. van Voorhis and K. T. Compton, the work of condensation of the electrons; and M. Pirani and H. Schönborn, electronic collision. J. A. M. van Liempt tried with good results the association of 0·1 to 3 per cent. of hafnia in place of thoria in tungsten lamp filaments.

W. A. Jenkins [8] found that slow-moving positive ions are emitted by tungsten when its temp. exceeds 2500°. R. L. Kenworthy, L. P. Smith, E. Meyer, E. T. S. Appleyard, H. B. Wahlin, and P. K. Mitra studied the emission of positive ions from hot tungsten filaments; and S. Kalandyk, from filaments in iodine vapour. C. Kenty and L. A. Turner observed that active nitrogen adsorbed by tungsten reduces the thermionic current. O. Stuhlman found that the minimum potential for the emission of secondary electrons is 372 volts, and R. L. Petry observed that secondary electronic emission occurred with the primary potentials, 11·0, 17·1, 25·2, 29·3, 40·5, 46·0, 89·5, and 271·5 volts; S. C. Roy found that the thermionic emission from tungsten between 1900° K. and 2700° K. is due to the photoelectric activity of the radiation from the bodies themselves. R. H. Whiddington discussed the velocity of the electrons liberated from tungsten by X-rays; A. G. Worthing, the pulsating thermionic discharge in evacuated tungsten lamps; H. E. Farnsworth, the electronic bombardment of tungsten surfaces; W. de Groot, the temp. and electronic emission of the tungsten arc; C. Davison and L. H. Germer, A. H. Warner, and T. H. Harrison, the thermionic work function; J. F. Congdon, the kinetic energy of the electrons from a hot tungsten filament; A. C. Davies and R. N. Moss, and N. B. Reynolds, the loss of thermionic activity by thoriated tungsten filaments; and R. Hamer, and H. Klumb, the photoelectric effect.

The visible and ultra-red **spectrum** of an incandescent tungsten wire at 2200° is continuous. The spectrum is plotted in Fig. 12—A. W. Hull.[9] The shaded portion represents the visible part. If the wave-lengths were all reduced ten-thousandfold, the curve would coincide very nearly with the dotted line in Fig. 13. J. N. Lockyer observed the lines 5514·9 and 5492·6 in the oxy-coal gas **flame spectrum.** The **spark spectrum** of tungsten was examined by W. A. Miller, R. Thalén, E. Demarçay, F. Exner and E. Haschek, A. Hagenbach and H. Konen, A. G. G. Leonard, H. W. Vogel, J. H. Pollok, H. B. Lemon, A. G. Worthing and R. Rudy, and J. M. Eder and E. Valenta. The chief lines are 5734 in the yellow; 5514, 5492, 5224, 5071, 5069, 5053, 5015, and 5008 in the green; 4888 and 4843 in the blue; and 4302, 4295, and 4269 in the indigo-blue. E. J. Allin and H. J. C. Ireton, and E. O. Hulbert discussed the spectrum of the spark in water; S. Smith, the spectra of electrically exploding wires; and C. Porlezza and A. Donati, the spectroscopic detection of tungsten. The **arc spectrum** was studied by J. N. Lockyer, M. Belke, W. J. Humphreys, C. C. Kiess and W. F. Meggers, A. Sellerio, F. Exner and E. Haschek, C. B. Hasselberg, O. Hagenbach and H. Konen, W. E. Forsythe and M. A. Easley, and J. M. Eder and E. Valenta; and the **ultra-**

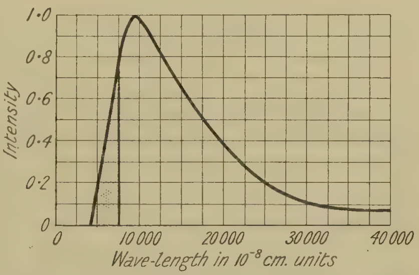


FIG. 12.—The Spectrum of Incandescent Solid Tungsten.

violet spectrum, by W. A. Miller, M. Bayen, O. Lohse, T. Aden, L. and E. Bloch, M. Lulkiesch, V. Schumann, and F. Exner and E. Haschek. According to W. H. Fulweiler and J. Barnes, the light from the tungsten arc under water gives a continuous spectrum in the ultra-violet. The **ultra-red spectrum** is discussed above. M. Luckiesh has shown that the ultra-violet spectrum of tungsten electrodes in quartz bulbs with argon may be considered for some purposes as approximately continuous between $300\mu\mu$ and $400\mu\mu$, although with short exposures the spectrum is fluted. The quartz mercury arc in this region emits many lines, but the spectrum does not approximate continuity. W. E. Forsythe and F. Christison calculated the energy of the ultra-violet spectra.

The influence of *pressure* on the spectrum was examined by W. J. Humphreys; and of a *magnetic field*—the **Zeeman effect**—by P. Zeeman, and R. Jack. H. B. Dorgelo studied the **absorption spectrum** of the vapour. No characteristic absorption spectrum of soln. of the tungsten salts has been observed, and J. Formanek observed no reaction with tincture of alkanna. J. H. Pollok examined the spectra of soln. of tungsten salts; and C. Horner, the spectra of beads of the oxide with boric acid, and phosphoric acid. A. de Gramont said that the lines 2397·110, 3215·578, 3613·793, 4008·769, and 4302·123 are *les raies ultimes*. No **series spectrum** has been observed, but E. Paulson has noted some pairs with constant differences. The subject was studied by P. G. Nutting, H. Beining, O. Laporte, and J. Stock. J. C. McLennan and co-workers discussed the relation between the electronic structure and the spectrum.

The **X-ray spectrum** of tungsten is continuous and it extends over four octaves, from the wave-length $0{\cdot}12 \times 10^{-8}$ cm. to 2×10^{-8} cm. The spectrum illustrated by Fig. 13 was obtained by A. W. Hull[10] with an ionization chamber and an electrometer-current 1·2 milliampères and 100,000 volts. The dotted line was obtained at 70,000 volts, and this was not high enough to excite the K-lines. The diagram represents four lines on the short wave-length end of the spectrum; they form the K-series, and are designated the α' and α doublet, β, and γ. Another group of about 12 lines with wave-lengths nearly ten times those of the K-series form the L-series. The X-ray spectrum was studied by M. de Broglie, P. Günther, J. Herweg, J. Barnes, K. T. Compton and C. H. Thomas, A. H. Compton, A. Smekal, E. Lorenz, A. W. Hull and M. Rice, W. S. Gorton, H. G. J. Moseley, etc. The K-series comprises the lines $\alpha_2\alpha$, 0·21352 A.; $\alpha_1\alpha_1$, 0·20885 A.; α_3, 0·215 A.; $\beta_1\beta$, 0·18436 A.; and $\beta_2\gamma$, 0·17940 A. The limit of the K-absorption is 0·1782 A. The K-series was studied by E. Dershem, W. Duane and co-workers, M. de Broglie, K. C. Mazumder, H. R. Robinson, S. K. Allison and W. Duane, C. B. Crofutt, M. C. Magarian, V. Posejpal, B. Walter, H. Purks, P. A. Ross, A. Bouwers, D. Coster, A. Leide, G. Réchou, C. D. Niven, A. Smekal, P. Auger, C. B. Crofutt, H. G. J. Moseley, J. E. Mack and J. M. Cork, J. M. Cork, B. R. Stephenson and J. M. Cork, F. K. Richtmyer, J. Thibaud and A. Soltan, O. B. Overn, M. Siegbahn, R. Ledoux-Lebard and A. Dauvillier, A. E. van Arkel and W. G. Byrgers, G. Agte and K. Becker, L. Y. Faust, etc. R. Berthold compared the ionizing and photographic effects of the K-series of X-rays. The L-series comprises the lines: $\alpha_2\alpha'$, 1·48452 A.; $\alpha_1\alpha_1$, 1·47348 A.; $\beta_1\beta$, 1·2791 A.; $\beta_2\gamma$, 1·24191 A.; $\gamma_1\delta$, 1·09553 A.; ϵ, 1·67505 A.; η, 1·4177 A.; $\beta_5\zeta$, 1·2118 A.; $\gamma_2\theta$, 1·06584 A.; $\beta_4\nu$, 1·29874 A.; $\beta_3\phi$, 1·26000 A.; $\gamma_3\chi$, 1·05965 A.; and $\gamma_4\psi$, 1·02647 A. The limits of the L-absorption are L_1, 1·2136 A.; L_2, 1·0726 A.; and L_3, 1·024 A. The L-series was studied by G. Wentzel, M. Siegbahn, C. D. Niven, H. Brauns, M. Siegbahn and E. Friman, E. Friman, F. C. Hoyt,

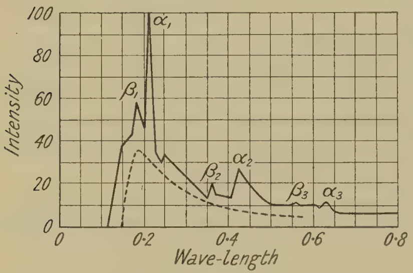


Fig. 13.—X-ray Spectrum of Tungsten (100,000 volts).

O. B. Overn, J. M. Cork, P. Kirkpatrick and I. Mayike, R. Ledoux-Lebard and A. Dauvillier, S. Idei, W. Duane and co-workers, J. S. Rogers, E. Hjalmar, D. Coster, M. de Broglie, E. Dersham, A. Smekal, H. R. Robinson and C. L. Young, E. C. Watson and J. A. van der Akker, Y. Nishina, B. B. Ray, C. B. Crofutt, S. K. Allison and A. H. Armstrong, H. Hirata, J. S. Rogers, U. Yoshida and S. Tanaka, A. Dauvillier, W. H. Love, J. Zahradnicek, A. Sandström, S. Idei, H. J. G. Moseley, etc. The M-series comprises the lines 4·433 A.; 5·167 A.; 5·356 A.; 5·607 A.; γ, 6·083 A.; 6·123 A.; 6·271 A.; β', 6·720 A.; β, 6·733 A., 6·750 A.; η_2, 6·789 A.; η, 6·857 A.; α', 6·948 A.; α, 6·963, 7·349 A., 9·549 A., and 8·948. The limits of the M-absorption are M_1, 6·708 A.; M_2, 6·475 A.; M_3, 5·416 A.; M_3', 5·380 A.; M_4, 4·800 A.; and M_5, 4·365 A. The M-series was studied by M. Thoræus, J. H. van der Tuuk, A. Jönsson, E. Lindberg, E. Lorenz, K. Molin, R. V. Zumstein, G. Wentzel, C. D. Niven, A. Jönsson, E. Hjalmar, M. Siegbahn, D. Coster, and A. Dauvillier; and the N-series and the O-series by C. T. Chu, J. A. Becker, E. Lorenz, C. D. Niven, and O. Stuhlman; and the P-series by C. D. Niven. W. Ehrenberg and co-workers studied the subject. W. Herz gave $5{\cdot}87\times10^6$ for the **vibration frequency.**

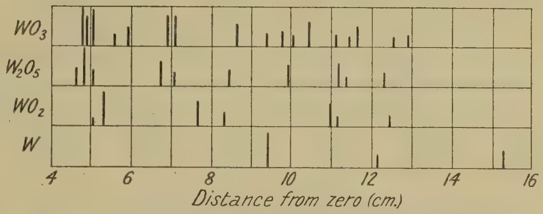


FIG. 14.—X-ray Diffraction Patterns of Tungsten and its Oxides.

C. J. Smithells and H. P. Rooksby's[11] X-ray diffraction patterns of tungsten and its oxides are given in Fig. 14. C. B. Bozzani and C. T. Chu obtained critical values for the X-rays from tungsten at 33·6, 34·6, 39·2, 56·6, and 71 volts. H. R. Robinson studied the secondary corpuscular rays produced by X-rays on tungsten; D. Nasledoff and P. Sharavsky, the intensity of the radiation from X-ray tubes; G. Kirsch and H. Pettersson, the action of α-rays; and G. B. Bandopadhyaya, the photoelectric action of soft X-rays; A. H. Warner, the photoelectric effect. T. E. Aurén found the at. absorption coefficient for X-rays to be 308 when that for lead is 569 and that for water is unity. V. Posejpal, L. M. Alexander, F. W. Warburton and F. K. Richtmyer, and S. J. M. Allen discussed this subject. S. K. Allison and W. Duane, A. H. Compton and A. W. Simon, F. Kirchner, G. Hagen, A. Claasen, and P. A. Ross discussed the scattering of X-rays by molybdenum, and the Compton effect; A. Jönsson, and A. Bouwers, the intensity of the X-rays; G. P. Thompson, the diffraction of cathode rays; G. L. Clark and W. Duane, the secondary and tertiary X-rays from tungsten; K. T. Compton and C. H. Thomas, O. W. Richardson and F. S. Robertson, and J. C. Boyce, the soft X-rays from tungsten; H. R. Robinson and A. M. Cassie, and R. Whiddington, the emission of electrons from tungsten bombarded by X-rays; W. H. Rothery, and R. A. Houstoun, the absorption of X-rays; J. A. Becker, the velocity of electrons exerted by X-rays; O. W. Richardson and co-workers, the excitation voltage of soft X-rays from tungsten; C. C. van Voorhis and K. T. Compton, the heats of condensation of electrons; and U. Nakaya, and L. P. Davis, the effect of oxidation on the emission of soft X-rays. M. de Broglie examined the α-ray spectrum. W. G. Guy observed no evidence of **radioactivity.** G. I. Pokrovsky, however, found evidence of radioactivity when the element is exposed to short-wave radiation—soft X-rays, and γ-rays. N. Koboseff and N. I. Nebressoff observed that free hydrogen atoms are produced by the cathodic polarization of tungsten; and J. K. Roberts discussed the energy between the atoms of helium and tungsten. O. W. Richardson and F. S. Robertson studied the **photoelectric effect;** and A. H. Warner found that the effect with tungsten is limited by a wave-length of 2570 A., and the limit is not affected by temp. up to 1140° K. R. B. Jones gave 2338 A. for the limiting wave-length. T. Pavolini studied the photoelectric effect; E. O. Lawrence and L. B. Linford, the effect with thin films of oxygen, and potassium on tungsten; and R. Suhrmann and F. Breyer, with a film of sodium on tungsten.

J. Lifschitz, and R. T. Dufford investigated the **volta-luminescence** which occurs when an electric current is passed through an electrolyte under certain conditions using tunsten electrodes. P. E. Shaw and C. S. Jex[12] found that when rubbed on glass, tungsten always acquires positive **triboelectricity.** M. Forro and E. Patai found the **contract potential** of sodium against tungsten to be 2·2 volts; I. Langmuir and co-workers measured the contact potentials of tungsten filaments against filaments with adsorbed cæsium; and N. B. Reynolds, the contact potentials of thoriated tungsten filaments.

The **electrical resistance** and the temp. coeff. of the resistance of tungsten wires varies with the different samples. O. Ruff found that rods, a metre long and 2 sq. mm. sectional area, made of the compressed powder and then heated to 2600° to 2650°, had a resistance $R=0{\cdot}5487+0{\cdot}0005144(\theta-1200)+0{\cdot}0_{6}2(\theta-1200)^2$, at a *temperature* between 1200° and 2940°. A. Müller found that a wire a metre long and 1 sq. mm. sectional area, had a resistance of 0·72 ohm. I. Langmuir gave $6{\cdot}37\times10^{-6}$ ohm at 0°, and $90{\cdot}34\times10^{-6}$ ohm at 2027°. For squirted filaments, unused, M. von Pirani gave $R=6\times10^{-6}$ to 12×10^{-6} ohm per cm. cube at 20°; and after being in use for 1000 hrs., $R=5{\cdot}5\times10^{-6}$ to $5{\cdot}7\times10^{-6}$ ohm at 20°. The temp. coeff. between 20° and 100° was 0·415 per cent. per degree. J. H. Dellinger found the sp. resistance of a squirted rod of tungsten, 20 cm. long, and 1·2 mm. diam., to be $0{\cdot}0_{5}63$ to $0{\cdot}0_{5}69$ ohm at 21·8°—this is nearly 4 times the resistance of copper. According to J. W. Avery and C. J. Smithells, the resistance falls rapidly in the early stages of working and reaches a minimum when the density is a maximum; it then increases at a uniform rate which is approximately an exponential function of the diameter.

A. G. Worthing gave for the resistance from 300° to the m.p., 3655°:

$T°$ K. .	300°	500°	1000°	1500°	2000°	2500°	3000°	3500°	3655°
$R\times10^6$	5·64	10·74	25·70	41·85	59·10	77·25	96·2	115·7	121·8

The results can be represented by the relation $R/R_0=(T/T_0)^{1\cdot2}$ between 1000° and 3200°, where R_0 denotes the resistance at 1000°. H. A. Jones gave the results R_1, and C. Zwikker, R_2:

$T°$ K. .	273°	500°	1000°	1500°	2000°	2500°	3000°	3500°	3655°
$R_1\times10^6$	5·00	10·56	24·90	40·35	56·67	73·83	92·00	111·1	117·1
$R_2\times10^6$	—	—	30·9(1200°)	40·2	56·7	74·0	92·3	107·8(3400°)	

H. Pécheux gave $18{\cdot}9\times10^4$ mho for the **electrical conductivity** at 0°; I. Langmuir, $20{\cdot}0\times10^4$ mho at 0°; and M. von Pirani, $17{\cdot}9\times10^4$ mho. For hard-drawn wires, C. G. Fink, and W. D. Coolidge gave for the resistance $R=0{\cdot}0_{5}62$ ohm at 25°, and after annealing, $0{\cdot}0_{5}50$ ohm at 25°—the temp. coeff. of the hard-drawn wire between 0° and 70° was 0·51 per cent. per degree; S. Weber gave $0{\cdot}0_{5}49$ at 0°, with a temp. coeff. of 0·46 per cent. between 0° and 23°. M. von Pirani observed no marked difference in the temp. coeff. of drawn and squirted wires at high temp. He found:

	−180°	0°	20°	100°	200°	500°	1000°	1500°	2000°
R .	$0{\cdot}0_{6}98$	$0{\cdot}0_{5}512$	$0{\cdot}0_{5}56$	$0{\cdot}0_{5}745$	$0{\cdot}0_{5}990$	$0{\cdot}0_{4}179$	$0{\cdot}0_{4}336$	$0{\cdot}0_{4}514$	$0{\cdot}0_{4}711$

From these measurements, O. M. Corbino calculated the temp. coeff. of the resistance R at $\theta°$ to be $\alpha=(dR/d\theta)/R$, or $\alpha=0{\cdot}00124$ at 800°; 0·00094 at 1050°; 0·00081 at 1250°; 0·00067 at 1450°; 0·00075 at 1800°; and 0·00076 at 1850°. A. Schulze gave $\alpha=0{\cdot}00413$ from 20° to 100°; 0·0050 from 400° to 800°; 0·0058 from 1000° to 1200°; and 0·009 up to 2000°. A. A. Somerville found at 25°, 100°, 500°, and 1000°, $\alpha=(dR/d\theta)/R_0$, the respective values 0·0046, 0·0050, 0·0057, and 0·0089, and his results for the resistance, and the temp. coeff. of the resistance are plotted in Fig. 15. P. W. Bridgman gave for the temp. coeff. 0·00322 between 0° and 100°; and L. Holborn gave for a wire 0·1 mm. in diameter which had been heated for a long time in vacuo, α=0·00435, 0·00465, and 0·00547, respectively at —135°, 50°, and 350°, and for the ratio of the resistance R at θ°, and R_0 at 0° :

	−78·3°	−80°	−100°	−120°	-140^0	−160°	−180°	−192·8°
R/R_0 . .	0·6509	0·644	0·557	0·469	0·382	0·295	0·208	0·1529

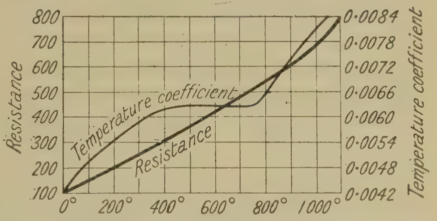


FIG. 15.—The Effect of Temperature on the Resistance of Tungsten.

W. Geiss and J. A. M. van Liempt gave for the sp. resistance of purified single crystals of tungsten, R=$0{\cdot}0_5491$ ohm., and the temp. coeff. 0·00481. The electrical conductivity is not affected by the orientation of the crystal, and the same values were obtained when the single crystals were converted by drawing and annealing into fine-grained metal. They found that the sp. resistance is increased 160 per cent. by the cold working of the metal, and the temp. coeff. of the resistance is reduced 60 per cent. The mixture law, that for solid soln., the product of the sp. resistance and the temp. coeff. remains constant, applies to a pure metal after working in the cold. The change in conductivity is not due to lattice modification, nor to change in orientation of atomic axes ; it is connected, as is also the change in mechanical properties, with the intercrystalline relations. By cold working, as also by taking up a solid soln. component, the energy content of a metal is increased : calculation from the electrical measurements indicates an increase of 775 cals. per gram atom of tungsten after cold working. F. Koref noted a change in the electrical resistance of single crystal wires by tempering. According to J. Tsukamoto, the sp. electrical resistance of drawn tungsten wire containing one per cent. of thorium, is dependent upon the fineness of the tungsten powder from which the wire was made, on the time of sintering, and on the temp. of drawing. At 20°, the sp. resistance of a rod, 0·47 cm. sq., is 6·1 microhms, which falls to a minimum of 5·7 microhms on drawing down to a diameter of 4·5 mm. Further drawing increases the resistance to 6·0 microhms at 0·35 mm. diameter, and to 7·1 microhms at 0·015 mm. diameter. J. C. McLennan and co-workers studied the conductivity at low temp., 2·2° K., and found the temperature-resistance curve to be normal. E. Grüneisen and E. Goens studied the relation between the electrical and thermal conductivities ; W. Geiss and J. A. M. van Liempt found that tungsten conforms with Matthiessen's rule as to the constancy of the product of the sp. resistance and the temp. coeff. of the resistance and for the ratio of the resistance R at θ°, and R_0 at 0°. B. Beckman measured the influence of *pressure ;* and P. W. Bridgman found for press., p, up to 12,000 kgrms. per sq. cm., and for temp. 0° to 100°, the press. coeff. of the resistance :

		0°	25°	50°	75°	1000°
	R . .	1·000	1·0743	1·1486	1·2229	1·2973
Press. Coeff.	0 kgrm. .	$-0{\cdot}0_51487$	$-0{\cdot}0_51497$	$-0{\cdot}0_51507$	$-0{\cdot}0_51518$	$-0{\cdot}0_51530$
	12,000 kgrms.	$-0{\cdot}0_51373$	$-0{\cdot}0_51399$	$-0{\cdot}0_51409$	$-0{\cdot}0_51426$	$-0{\cdot}0_51442$
	average .	$-0{\cdot}0_51430$	$-0{\cdot}0_51444$	$-0{\cdot}0_51458$	$-0{\cdot}0_51472$	$-0{\cdot}0_51486$

E. D. Williamson gave 0·9838 for the ratio of the resistance at pressures of 12,000 kgrms. and 1 kgrm. per sq. cm. U. Fischer found for the effect of pressure on the resistance $-(1/R)(dR/dp)$, at 15°, 0·1°, —185°, and —252·7°, the respective values $0{\cdot}0_5159$, $0{\cdot}0_5155$, $0{\cdot}0_528$, and $0{\cdot}0_5495$. H. Rolnick found that under a *tensile stress* the fractional change of resistance is $\delta R/R$=0·000194. R. Becker and F. Born found a difference of less than 5 per cent. in the conductivity parallel and perpendicular to the direction of rolling. G. Tammann and M. Staumanis discussed the effect of cold work on the electric resistance ; A. Denissov, the effect of the electric current on the temp. of a thin wire ; the effect of the press. of hydrogen on the electrical resistance of a filament; and P. Kapitza, the effect of a magnetic field on the electrical conductivity. K. Höjendahl, A. T. Waterman, and O. Feussner discussed the electronic theory of conductivity. S. Smith measured the conductivity of the vapour of tungsten. I. Langmuir and co-workers calculated the losses at the leads of tungsten filament lamps.

A. G. Worthing, in his study of the effect of the direction of the heating current on the temp. variation near a leading in wire of a tungsten filament lamp, measured the thermoelectric force—the **Thomson effect**—and found for the Thomson effect at 1800°, 2000°, and 2200° in microvolts per degree, respectively, −18, −22, −26, and −30. Tungsten appears to be the only known metal with a positive temp. coeff. for the Thomson effect, σ. C. Zwikker gave for the Thomson effect in millivolts per degree:

T° K.	1800°	1900°	2000°	2100°	2200°	2300°	2400°
σ .	−18	−20	−22	−24	−26	−28	−30

P. W. Bridgman found the Thomson effect with a couple composed of one branch of uncompressed metal, and the other compressed at p kgrms. per sq. cm., to be, in joules per coulomb × 10 per degree of temp.:

	p	0°	40°	80°	100°
σ	2,000 .	2·0	2·3	2·6	2·8
	6,000 .	8·5	7·8	6·5	5·6
	10,000 .	3·5	10·2	18·7	23·5
	12,000 .	9·3	13·1	17·3	19·8

The positive effect at the two extremes of press. rises with temp. at a constant press., but at intermediate press. it rises and falls with a rise of temp. H. E. Smith measured the effect of tension on the Thomson effect in a tungsten wire, and he found that the coeff. increases with tension, but when the stress is relieved, the original value is not restored even though the stress is below the elastic limit; the coeff. undergoes a regular cycle of changes with a repeated application and removal of the stress, Fig. 16. With tungsten of 99·95 per cent. purity, and a tension expressed in dynes per sq. cm., the Thomson effect, σ, expressed in cals. per coulomb per degree, is:

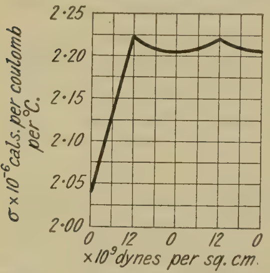


FIG. 16.—The Effect of Tension on the Thomson Effect.

Tension × 10^9	0	2·95	5·90	8·85	11·80 dynes
$\sigma \times 10^6$.	2·038	2·079	2·106	2·163	2·222 cals.

P. W. Bridgman found the Thomson effect against lead, at atm. press., to be represented by $\sigma=0·0341(\theta+273)10^{-6}$ volts per degree. The **Peltier effect,** P, joules per coulomb × 10^6, between compressed and uncompressed tungsten, rises with temp. and press.:

	p	0°	40°	80°	100°
P	2,000 . .	5·9	7·7	9·5	10·4
	6,000 . .	17·2	23·1	29·0	32·0
	10,000 . .	30·4	37·5	48·3	55·4
	12,000 . .	35·7	45·9	58·0	64·8

The value with the tungsten-lead couple is $p=(1·594+0·0341\theta)/(\theta+273)\times10^{-6}$ volt. P. W. Bridgman found the **thermoelectric force** of a couple, E, composed of compressed and uncompressed tungsten, for values of the press. up to 12,000 kgrms. per sq. cm., to be positive; and is about 20 times as great as the value for molybdenum; the thermoelectric force also increases regularly with press. and temp. Expressing the thermoelectric force E in volts × 10^{-6}:

	p	0°	40°	80°	100°
E	2,000 . .	0·22	0·94	1·98	2·53
	6,000 . .	0·65	2·76	5·92	7·60
	10,000 . .	1·12	4·61	9·75	12·61
	12,000 . .	1·33	5·56	11·76	15·41

The thermoelectric force of the *tungsten-lead* couple is $E=(1\cdot594\theta+0\cdot01705\theta^{2})10^{-6}$ volt. W. W. Coblentz obtained for the thermoelectric force, E microvolts, for the *tungsten-copper* couple, a maximum value for E in the curve at 40° :

	−200°	−100°	0°	20°	40°	100°	150°	200°	250°
E .	−600	−240	0	20	22	−38	−160	−340	−590

W. M. Latimer found the thermoelectric force of the *tungsten-silver* couple to be —2·5 microvolts at 100° ; —6·0 at 200° ; —9·2 at 400° ; and —9·8 at 700°. E. Blumenthal found the Peltier effect for tungsten against molybdenum to be $4\cdot69\times10^{-3}$ gram cal. at ordinary temp., and $29\cdot3\times10^{-3}$ gram cal. at 1017°. W. Rohn studied the thermoelectric force of tungsten against nickel. S. Morugina gave for the thermoelectric force of the *tungsten-tantalum* couple 10·3 millivolts at 1060° ; 16·0, at 1520° ; the *tungsten-molybdenum* couple, S. Morugina gave —3 millivolts at 1000° and at 1500° ; and 1·5 millivolts at 2000°. A. G. Worthing also studied the tungsten-tantalum couple—*vide* tantalum. E. F. Northrup found the thermoelectric force of the *tungsten-molybdenum* couple, E microvolts, between 0° and 1000° to be represented by $E=4\cdot61\theta-0\cdot00436\theta^{2}$, with, at most, a 4 per cent. error. The value of E decreases up to 530°, and then rises, being about the same as at 0° near 1150°, so that at this temp. the direction of the current is the opposite to what it is at 0°—*vide* Fig. 17. Below that temp., at the hot junction, the current flows from the tungsten to the molybdenum. The high m.p. of tungsten makes it valuable in the construction of thermocouples for high temp., but they can be employed only in the presence of a reducing atmosphere—say hydrogen, or a mixture of hydrogen and nitrogen. M. von Pirani and G. von Wangenheim used a couple of tungsten against an alloy of molybdenum with 75 per cent. of tungsten to measure the m.p. of molybdenum. It could be used up to 3000° ; below 1600°, the current at the hot junction flows from the tungsten to the alloy, and reaches a maximum of about one millivolt at about 600° ; at 1200°, the current reverses and reaches 6 millivolts at 3000°. G. Borelius found that the thermoelectric force of the iron-tungsten couple at ordinary temp., with tungsten which had been successively heated at different temp., and each time rapidly cooled, shows periodic changes when the e.m.f. is taken as a function of the heating temp. R. Saxon found that when a piece of tungsten is placed between, but not touching, two electrodes immersed in water and a current is passed between the electrodes, the surface of the intermediate metal remains bright on the side nearest the cathode, but becomes oxidized on the side nearest the anode, whilst, in some cases, a mixture of oxygen and hydrogen in the ratio of <1 : 2 is evolved.

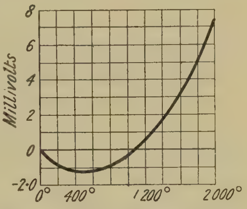


Fig. 17.—The Thermoelectric Force of a W–Mo Couple.

R. D. Kleeman and W. Frederickson [13] found that in distilled water, tungsten assumes a negative charge when an electric current is sent through the liquid. A. S. Russell and S. W. Rowell said that the position of tungsten in the electrochemical series is approximately the same as that of molybdenum (*q.v.*). H. H. Willard and F. Fenwick examined tungsten as an electrode material. According to W. Muthmann and F. Fraunberger, active tungsten, like iron and chromium, can assume a **passive state,** although in some respects the behaviour of tungsten is different from that of chromium. Its electrode potential is not a constant, but is dependent on the treatment the metal has previously received. Tungsten is made passive by treatment with the oxidizing agents, chromic acid, nitric acid, and ferric chloride, as well as by hydrochloric and sulphuric acids. The highest **electrode potential** which passive tungsten can receive by treatment with chromic acid, is 0·88 volt in a N-soln. of potassium chloride ; in air, the potential ranges from 0·35 volt to —0·03 volt. The metal is activated by polishing, and its potential is then —0·58 volt ; and this can be raised to —0·70 volt by cathodic polarization in water. Cathodic polarization in acids or in alkali-lye also activates the passive metal. With a tungsten anode and platinum cathode, M. le Blanc and H. G. Byers found that when sulphuric, hydrochloric, and nitric acids in normal soln. are used as electrolytes, tungsten is practically unattacked. In soln. of phosphoric acid and of sodium hydrophosphate at high temp., it dissolves in the sexivalent form; at low temp., however, the current efficiency is smaller. In oxalic acid with small currents and at high temp., the current efficiency reaches the theoretical value, but is much less with relatively large currents at room temp. The current efficiency also approximates to the theoretical value in normal soln. of potassium hydroxide and of ammonium sulphide. The change from the active to the passive (relatively insoluble) form of the metal is favoured by increasing the current density and by lowering the temp. They say it is improbable that the passivity is conditioned by the formation of a layer on the surface of the metal; it is more likely to be connected with a change in the reaction velocity. L. B. Flexner and E. S. G. Barron measured the potential of the tungsten electrode in various oxidation-reduction systems. M. Katalinic observed a faint luminescence about a tungsten anode in conc. sulphuric acid at voltages exceeding 60. A. Thiel and W. Hammerschmidt found the **over-voltage** with tungsten and $2N$-H_2SO_4 to be 0·157 volt at 25°. S. J. French and L. Kahlenberg studied the gas-metal electrode with tungsten and oxygen, hydrogen, or nitrogen.

According to E. Newbery, tungsten under anodic treatment in dil. sulphuric acid, dissolves readily and shows no signs of passivity. The surface acquires a very brilliant, polished appearance. In alkali-lye, it behaves in the same way as bismuth. O. Sackur discussed the passivity of tungsten. W. E. Koerner found that tungsten dissolves anodically in aq. soln. of ammonium hydroxide, or hydroxylamine; in methyl-, ethyl-, and propyl-ammonium hydroxides to form the respective paratungstates; and at high current densities the tungsten becomes passive. Tungsten also dissolves anodically in aq. soln. of potassium and sodium hydroxides to form orthotungstates; and it becomes passive with high current densities. Tungsten dissolves in non-aqueous soln. of hydrochloric acid, potassium chloride or fluoride, sodium chloride, etc., forming the respective halogen salts without becoming passive; and it dissolves to a slight extent in aq. soln. of hydrochloric, sulphuric or nitric acid, and potassium fluoride, chloride, bromide or iodide with the formation of tungsten hexahydroxide, but the metal becomes passive. The metal remains active only at very low current densities.

The passivity of tungsten is due to oxide films, ranging in colour from brown, blue and green to yellow. The colours are pronounced and can be followed as the electrolysis proceeds. The films are independent of the dissolved cation or anion. They are due to the OH-ions reacting with the tungsten. The passivity is a function of the colour of the film, the colour varying with the amount of oxygen present. The passivity varies directly with the current, time and temp., and inversely with the solubility of the film, the vol. of electrolyte and the diffusion velocity. If the film dissolves as rapidly or more rapidly than it is formed, the tungsten will remain active. The films can be dissolved and the passivity destroyed. Soln. of potassium hydroxide and ammonia render passive tungsten active. Soln. of acids and salts make passive tungsten active if allowed to react for some time on it. Passive tungsten has been made active overnight in distilled water. I. Langmuir and K. H. Kingdon studied the contact potential differences between a clean, unheated tungsten filament, and the same filament coated with a film of thorium, cæsium, or oxygen.

In conjunction with the anodic soln. of tungsten, the electrochemical eq. was determined. Tungsten dissolves sexivalently in a soln. of ammonia with 100 per cent. efficiency. From the loss in weight of a tungsten anode in ammonia and the coulombs of current, the **electrochemical equivalent** was found to be 0·3173 mgrm. per coulomb—the theoretical value is 0·3175 mgrm. per coulomb.

W. E. Koerner found the single electrode potential of tungsten in normal soln., referred to the standard hydrogen electrode, to be —0·656 volt for KCy; —0·315 volt for KOH; —0·238 volt for NH_4OH; 0·193 volt for H_2SO_4; 0·256 volt for HCl; 0·311 volt for HNO_3; 0·522 volt for KF; 0·053 volt for KCl; 0·589 volt for KBr; and 0·733 volt for KI. The electrode potential varies with the nature of the electrolyte. The metal is negative to the electrolyte with soln. of the bases; and positive with acid and salt soln. The soln. tension or solubility of a metal in an electrolyte is a function of the electrode potential; and the solubility therefore is greatest in soln. of the bases, and least in soln. of salts. Tungsten is more soluble in soln. of potassium cyanide than of the hydroxide; and more soluble in potassium hydroxide than in aq. ammonia; it is more soluble in sulphuric acid than in hydrochloric acid, and more soluble in hydrochloric acid than in nitric acid. The order of solubility in soln. of the salts—KF, KCl, KBr, and KI—is in order named. O. Bauer gave for the potential of tungsten against a one per cent. soln. of sodium chloride and a normal calomel electrode, —0·260 volt at the start falling to —0·235 volt in 1 hr., and —0·240 volt in 120 hrs. A. Fischer and co-workers measured the electromotive force of the cell with tungsten in an alcoholic soln. of tungsten hexachloride, against a calomel electrode in contact with an alcoholic soln. of lithium chloride, and found for soln. with one-sixth mol of the hexachloride in v litres:

v .	1·30	2·82	5·82	9·84	123	417	925
E.m.f.	0·504	0·492	0·474	0·465	0·399	0·362	0·349 volt.

They calculated the normal potential of tungsten in an alcoholic soln. of sexivalent tungsten to be 0·68 volt; and in aq. soln., 0·61 volt. These values are based on questionable assumptions. They infer that tungsten is nearly as noble a metal as silver; and in the electrochemical series, tungsten occupies a place between antimony and mercury. Passivity was not observed. W. E. Koerner obtained normal soln. of tungsten hexahydroxide in sulphuric, hydrochloric and nitric acids by electrolyzing the acids at low current densities between tungsten electrodes. Measurements of the e.m.f. of cells were made with tungsten in a N-soln. of the acid, and with tungsten in a sat. soln. of tungsten hexahydroxide. These combinations were concentration cells with the conc. of the hexahydroxide zero. With $W^+ \mid H_2SO_4$; $W(OH)_6 \mid H_2SO_4 \mid W^-$, the e.m.f. was 0·117 volt.; with HCl in place of H_2SO_4, 0·057 volt; and with HNO_3 in place of H_2SO_4, 0·009 volt. Hence, tungsten hexahydroxide is most soluble in sulphuric acid, and least soluble in nitric acid. True soln., not colloidal soln., are formed; and tungsten occurs in the cation.

O. W. Richardson and F. S. Robertson found that the voltage-current curve between a hot tungsten filament and mercury vapour is shifted to the negative along the voltage-axis by increasing the press. of hydrogen. This change is taken to represent the contact difference of potential as influenced by the gas press. W. E. Koerner showed that tungsten is negative to soln. of the bases so that voltaic cells are formed if it be combined with a metal—*e.g.* mercury or silver—positive to these soln., with N-NaOH sat. with mercuric oxide, the potential of mercury is 0·168 volt (hydrogen zero); and with the N-NaOH sat. with silver oxide, the potential of silver is 0·378 volt (hydrogen zero); and with the tungsten employed in the experiments, the electrode potential in N-NaOH is —0·704 volt (hydrogen zero). A cell with tungsten and mercury in N-NaOH sat. with mercuric oxide has an e.m.f. of 0·872 volt—the mercury being positive; similarly with tungsten and silver in N-NaOH sat. with silver oxide, the e.m.f. is 1·082 volt, the silver being positive. If $10N$-NaOH be used with the mercury-tungsten combination, the e.m.f. is 1·050 volt. The e.m.f. with the cell $Hg^+ \mid Hg_6W_7O_{24} \mid Na_6W_7O_{24} \mid W^-$ is 0·552 volt; with $Cu^+ \mid Cu_3W_7O_{24} \mid Na_6W_7O_{24} \mid W^-$, 0·395 volt; and with $Cd^- \mid Cd_3W_4O_{24}Na_6W_7O_{24} \mid W^-$, 0·434 volt. Experiments were made with storage cells having tungsten and tungstic acid for the positive electrode and tungsten for the negative electrode, and sulphuric acid as electrolyte. The e.m.f. before charging was 0·08 volt, and after charging 3·00 volts; 24 hrs. after charging the e.m.f. had dropped to 0·2 volt. No change of colour was observed. The best combination tried had, before charging, tungsten as positive electrode and tungsten and tungstic acid as negative electrode. During charging the yellow tungsten acid was reduced through a series of coloured oxides to a blue-black compound, probably W_2O_5. The tungsten of the positive electrode became covered with a brown film, presumably WO_2. Before charging, the e.m.f. 0·08 volt was observed; and immediately after charging the e.m.f. was as high as 6·20 volts. This value did not remain constant because, 24 hours after charging, 0·75 volt was obtained. This value remained constant for two weeks. A. L. Clark studied the polarization capacity of tungsten. L. W. Walter, and A. Günther-Schulze observed that with many electrolytes, tungsten shows the **electrolytic valve action**; the critical voltage with strong acids is, as a rule, higher than with aluminium, and not so high as with tantalum. This rectification of alternating currents by tungsten was discussed by S. Dushman, R. E. Russell, and G. S. Meikle; the cathodic disintegration, by E. Blechschmidt; the surface pitting of tungsten filaments, by E. S. Davenport; contact potential with adsorbed films, by I. Langmuir and K. H. Kingdon; the tungsten arc, by W. B. Nottingham, S. H. Anderson and G. G. Kretchmar, W. B. Nottingham, W. de Groot, and W. Wehrli; electrokinetic potential, by A. Coehn and O. Schafmeister; C. del Rosario, and J. Taylor, the sparking potentials of discharge tubes with tungsten electrodes; P. Bächtiger, the tungsten arc; and H. Nagaoka and T. Futagami, the spluttering of tungsten by the disruptive discharge in a magnetic field. E. K. G. Stückelberg said that the temp. of the tungsten cathode in an electric arc is 2600° to 3300° K. J. S. Forrest discussed the glow discharge on the active electrode of a rectifying cell.

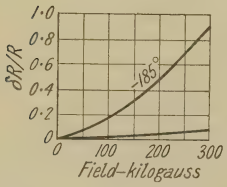


Fig. 18.—The Effect of Magnetic Fields on the Electrical Conductivity.

According to H. Moissan,[14] tungsten is not ferromagnetic; but is paramagnetic. L. Weiss also said that the metal is non-magnetic. K. Honda gave $0·33\times10^{-6}$ for the **magnetic susceptibility** between 18° and 1100°; while M. Owen obtained for the metal, free from iron, $0·252\times10^{-6}$ in a magnetic field of 26 kilograms; and $0·222\times10^{-6}$ for an infinitely strong magnetic field. The result is independent of the temp. Some observations on this subject were made by S. Meyer; and by D. M. Bose and H. G. Bher. P. Kapitza's observations on the effect of magnetic fields on the electrical conductivity are summarized in Fig. 18.

References.

[1] S. Ohashi, *Nagaoka Anniv. Vol.*, 417, 1925; J. J. and F. de Elhuyar, *Análisis quimico del volfram y exámen de un nuovo metal que entra en su composicion*, Bascongada, 1783; *A Chemical Examination of Wolfram and Examination of a New Metal which enters into its Composition*, London, 1785; *Chemische Zerkliederung des Wolframs*, Halle, 1786; *Mém. Acad. Toulouse*, **2**. 141, 1784; G. A. Meierson, *Journ. Russ. Phys. Chem. Soc.*, **60**. 1217, 1928; F. Wöhler, *Pogg. Ann.*, **2**. 345, 1824; *Quart. Journ. Science*, **20**. 177, 1826; *Phil. Mag.*, **66**. 263, 1825; *Gött. Nachr.*, 35, 1850; *Liebig's Ann.*, **73**. 190, 1850; **77**. 262, 1851; *Ann. Chim. Phys.*, (2), **29**. 43, 1823; (3), **29**. 187, 1850; E. Zettnow, *Pogg. Ann.*, **130**. 16, 241, 1867; P. Debye, *Phys. Zeit.*, **18**. 483, 1917; M. Ettisch, M. Polanyi and K. Weissenberg, *ib.*, **22**. 646, 1921; *Zeit. phys. Chem.*, **99**. 332, 1921; *Zeit. Physik*, **7**. 181, 1921; W. P. Davey, *Journ. Amer. Opt. Soc.*, **5**. 479, 1921; *Gen. Elect. Rev.*, **25**. 565, 1922; *Phys. Rev.*, (2), **23**. 292, 1924; H. P. and W. P. Davey, *ib.*, (2), **31**. 160, 1928; (2), **25**. 736, 753, 1925; (2), **26**. 736, 1925; A. W. Hull, *ib.*, (2), **17**. 376, 1921; A. W. Hull and W. P. Davey, *ib.*, (2), **17**. 571, 1921; H. C. Burger, *Zeit. Physik*, **58**. 11, 1929; *Phys. Zeit.*, **23**. 14, 1922; *Physica*, **2**. 114, 1922; A. E. van Arkel, *ib.*, **3**. 76, 1923; **5**. 208, 1925; C. F. Bucholz, *Schweigger's Journ.*, **3**. 1, 1811; F. S. Goucher, *Phil. Mag.*, (6), **48**. 229, 1924; (7), **2**. 289, 1926; *Brit. Pat. No.* 181703, 9102; J. Leonhardt, *Zeit. Kryst.*, **63**. 478, 1926; C. J. Smithells and H. P. Rooksby, *Nature*, **120**. 226, 1927; C. J. Smithells, H. P. Rooksby, and W. R. Pitkin, *Journ. Inst. Metals*, **36**. 107, 1926; E. Sutter, *Die Entstehung von Eisenkristallen und ihre Wachstumsbedingungen mit Berücksichtigung der Vörgänge bei der allotropen Umwandlung*, Griefswald, 1926; C. J. Smithells, *Tungsten*, London, 57, 1926; *Journ. Inst. Metals*, **27**. 107, 1922; *Trans. Faraday Soc.*, **17**. 485, 1921; R. Gross and N. Blassmann, *Neues Jahrb. Min. B.B.*, **42**. 728, 1919; B. Schmidt, *Phys. Ber.*, **6**. 610, 1926; *Aetz- und Lösungs-erscheinungen an Wolfram*, Greisswald, 1924; L. P. Sieg, *Phys. Rev.*, (2), **19**. 273, 1922; C. W. Siemens and A. K. Hunting-

ton, *Chem. News*, **46**. 163, 1882; K. Becker, *Zeit. Physik*, **42**. 226, 1927; **51**. 481, 1928; W. Braunbek, *ib.*, **38**. 549, 1926; W. G. Burgers, *ib.*, **58**. 11, 1929; R. Gross, F. Koref and K. Moers, *ib.*, **22**. 317, 1924; J. Hengstenberg and H. Mark, *Naturwiss.*, **17**. 443, 1929; Z. Jeffries, *Chem. Met. Engg.*, **16**. 503, 1917; *Trans. Amer. Inst. Min. Eng.*, **56**. 571, 1916; **60**. 588, 1919; **70**. 303, 1924; Z. Jeffries and R. S. Archer, *The Science of Metals*, New York, 86, 1924; *Chem. Met. Engg.*, **26**. 343, 1922; H. E. Roscoe, *Liebig's Ann.*, **162**. 359, 1872; *Proc. Manchester Lit. Phil. Soc.*, **11**. 79, 1872; *Chem. News*, **25**. 61, 73, 90, 1873; *Bull. Soc. Chim.*, (2), **25**. 61, 1873; J. J. Berzelius, *Schweigger's Journ.*, **16**. 476, 1816; *Ann. Phil.*, **3**. 245, 1814; *Ann. Chim. Phys.*, (2), **17**. 13, 1821; *Pogg. Ann.*, **4**. 147, 1825; **8**. 147, 267, 1826; H. von Wartenberg, *Ber.*, **40**. 3287, 1907; *Zeit. angew. Chem.*, **24**. 2433, 1911; H. Alterthum, *Zeit. phys. Chem.*, **110**. 1, 1924; *Zeit. Metallkunde*, **16**. 319, 1924; **19**. 121, 1927; E. Schmid, *ib.*, **20**. 370, 1928; E. Schiebold, *ib.*, **16**. 462, 1924; F. Koref, *ib.*, **15**. 47, 1923; **17**. 214, 1925; *Zeit. Elektrochem.*, **28**. 515, 1922; F. Skaupy, *ib.*, **33**. 487, 1927; F. Sauerwald, *Zeit. anorg. Chem.*, **22**. 277, 1922; M. E. Pennington and F. E. Smith, *ib.*, **8**. 198, 1895; L. Weiss, *ib.*, **65**. 334, 1910; G. Tammann and M. Straumanis, *ib.*, **169**. 365, 1928; J. A. M. van Liempt, *ib.*, **129**. 263, 1923; **195**. 366, 1931; W. Geiss and J. A. M. van Liempt, *ib.*, **143**. 259, 1925; *Ann. Physik*, (4), **77**. 105, 1925; *Zeit. Physik*, **45**. 631, 1927; H. Wolff, *Einfluss der Kristallformen und Kristallgrössen auf den thermodynamischen Inhalt, die Dichte und die Formbeständigkeit der Wolframdrähte*, Danzig, 1924; F. Koref and H. Wolff, *Zeit. Elektrochem.*, **28**. 477, 1922; T. Fujiwara, *Mem. Coll. Kyoto*, **11**. 283, 1928; **13**. 109, 149, 1930; W. Hume-Rothery, *Phil. Mag.*, (7), **10**. 217, 1930; J. Leonhardt, *Zeit. Kryst.*, **76**. 252, 1930; T. Fujiwara, *Mem. Coll. Kyoto*, **13**. 109, 1930; W. Rosenhain, *Inst. Internat. Phys. Solvay*, **4**. 155, 1927; J. Hengstenberg, *Metallwirtschaft*, **9**. 465, 1930.

[2] J. J. and F. de Elhuyar, *Análisis quimico del volfram y exámen de un nuovo metal que entra en su composicion*, Bascongada, 1783; *A Chemical Examination of Wolfram and Examination of a New Metal which enters into its Composition*, London, 1785; *Chemische Zerkliederung des Wolframs*, Halle, 1786; *Mém. Acad. Toulouse*, **2**. 141, 1784; H. C. Burger, *Physica*, **2**. 114, 1922; A. Riche, *Ann. Chim. Phys.*, (3), **50**. 33, 1857; J. Laissus, *Rev. Mét.*, **24**. 345, 1927; E. Zettnow, *Pogg. Ann.*, **130**. 16, 241, 1867; P. Vinassa, *Gazz. Chim. Ital.*, **58**. 178, 1928; F. A. Bernoulli, *Pogg. Ann.*, **111**. 570, 1860; *Chem. News*, **5**. 116, 1862; C. F. Bucholz, *Schweigger's Journ.*, **3**. 1, 1811; W. Allen and A. Aiken, in A. and C. R. Aiken, *Dictionary of Chemistry*, London, **2**. 445, 1807; L. von Uslar, *Gött. Nachr.*, **94**. 255, 1855; *Beiträge zur Kenntniss des Wolframs und Molybdäns*, Göttingen, 1855; H. E. Roscoe, *Liebig's Ann.*, **162**. 359, 1872; *Proc. Manchester Lit. Phil. Soc.*, **11**. 79, 1872; *Chem. News*, **25**. 61, 73, 90, 1873; *Bull. Soc. Chim.*, (2), **25**. 61, 1873; A. Stavenhagen, *Compt. Rend.*, **127**. 755, 1898; *Ber.*, **32**. 1513, 3064, 1899; S. M. Delepine, *Compt. Rend.*, **131**. 184, 1900; *Bull. Soc. Chim.*, (3), **23**. 675, 1900; H. von Wartenberg, *Ber.*, **40**. 3287, 1907; E. Donath and J. Mayrhofer, *ib.*, **16**. 1588, 1883; L. A. Hallopeau, *Bull. Soc. Chim.*, (3), **19**. 997, 1898; (3), **21**. 266, 1899; *Compt. Rend.*, **127**. 755, 1899; *Ann. Chim. Phys.*, (7), **19**. 115, 1900; A. Berkenheim, *Zeit. phys. Chem.*, **141**. 35, 1929; V. M. Goldschmidt, *Skr. Norske Vid. Akad.*, **2**, 1926; L. Pauling, *Journ. Amer. Chem. Soc.*, **49**. 765, 1927; E. T. Wherry, *Amer. Min.*, **14**. 54, 1929; H. Moissan, *Ann. Chim. Phys.*, (7), **8**. 570, 1896; *Le four électrique*, Paris, 229, 1897; London, 159, 1904; *Compt. Rend.*, **73**. 13, 1872; **116**. 1225, 1893; **123**. 13, 1896; L. Weiss, *Zeit. anorg. Chem.*, **65**. 279, 1910; G. Grube and K. Schneider, *ib.*, **168**. 17, 1927; I. Traube, *ib.*, **8**. 12, 1895; M. E. Pennington and E. F. Smith, *ib.*, **8**. 198, 1895; E. F. Smith and F. F. Exner, *Chem. News*, **90**. 66, 1904; *Journ. Amer. Chem. Soc.*, **26**. 1082, 1904; G. Arrivant, *Compt. Rend.*, **143**. 594, 1907; C. J. Smithells, *Tungsten*, London, **82**. 1926, *Journ. Inst. Metals*, **27**. 107, 1922; *Trans. Faraday Soc.*, **17**. 485, 1921; J. W. Avery and C. J. Smithells, *Proc. Phys. Soc.*, **39**. 85, 1926; C. J. Smithells, H. P. Rooksby and W. R. Pitkin, *Journ. Inst. Metals*, **36**. 107, 1926; F. S. Goucher, *Phil. Mag.*, (6), **48**. 229, 1924; (7), **2**. 289, 1926; L. Vegard, *ib.*, (7), **1**. 1151, 1925; C. G. Fink, *Trans. Amer. Electrochem. Soc.*, **22**. 499, 1912; *Met. Chem. Engg.*, **8**. 341, 1910; *Chem. News*, **104**. 34, 1911; A. G. Worthing and W. E. Forsythe, *Phys. Rev.*, (2), **18**. 144, 1921; *Astrophys., Journ.*, **61**. 146, 1925; A. G. Worthing, *ib.*, **36**. 345, 1912; *Journ. Franklin Inst.*, **181**. 857, 1916; *Phys. Rev.*, (2), **5**. 445, 1915; (2), **10**. 377, 638, 1917; (2), **12**. 199, 1918; W. Schriever, *ib.*, (2), **20**. 96, 1922; (2), **23**. 255, 1924; I. Langmuir, *ib.*, (2), **7**. 302, 1916; M. L. Huggins, *ib.*, (2), **28**. 1086, 1926; E. C. Bain and Z. Jeffries, *Chem. Met. Engg.*, **25**. 775, 1921; Z. Jeffries and R. S. Archer, *The Science of Metals*, New York, 216, 1924; Z. Jeffries, *Chem. Met. Engg.*, **16**. 503, 1917; *Trans. Amer. Inst. Min. Eng.*, **56**. 571, 1916; **60**. 474, 588, 1919; F. Koref, *Zeit. tech. Physik*, **7**. 544, 1926; *Zeit. Metallkunde*, **15**. 47, 1923; **17**. 214, 1925; *Zeit. Elektrochem.*, **28**. 515, 1922; W. Geiss, *Physica*, **3**. 322, 1923; *Zeit. Physik*, **29**. 78, 1924; *Zeit. Metallkunde*, **15**. 297, 1923; W. Geiss and J. A. M. van Liempt, *Zeit. anorg. Chem.*, **168**. 147, 1927; *Ann. Physik*, (4), **77**. 105, 1925; *Zeit. Physik*, **45**. 631, 1927; H. Achönborn, *ib.*, **8**. 377, 1921; J. Königsberger, *ib.*, **40**. 729, 1926; E. Grüneisen, *Ann. Physik*, (4), **22**. 811, 1907; L. P. Sieg, *Proc. Iowa Acad.*, **28**. 95, 1921; *Phys. Rev.*, (2), **9**. 337, 1916; (2), **25**. 251, 1925; J. M. Eglin, *ib.*, (2), **31**. 1127, 1928; P. W. Bridgman, *Proc. Amer. Acad.*, **58**. 166, 1923; **60**. 305, 1925; *Proc. Nat. Acad.*, **10**. 411, 1924; T. W. Richards and E. P. Bartlett, *Journ. Amer. Chem. Soc.*, **37**. 470, 1915; T. W. Richards, *ib.*, **46**. 1419, 1924; **47**. 731, 1925; **48**. 3063, 1926; L. H. Adams, *Journ. Washington Acad.*, **17**. 529, 1927; J. Waddell, *Zeit. phys. Chem.*, **3**. 491, 1889; J. R. Rydberg, *ib.*, **33**. 353, 1900; H. G. Grimm, *ib.*, **122**. 177, 1926; P. Hidnert and W. T. Sweeney, *Thermal Expansion of Tungsten*, Washington, 1925; *Scient. Papers Bur. Standards*, 515, 1925; H. Schröder, *Liebig's Ann.*, **173**. 71, 1874; W. Widder, *Phys. Zeit.*, **26**. 618, 1925; E. Ruhstrat,

Brit. Pat. No. 23437, 1910; *Elect. World,* **56**. 1311, 1910; E. W. Engel, *Trans. Amer. Inst. Min. Eng.*, **71**. 691, 1925; H. L. Dodge, *Phys. Rev.*, (2), **11**. 311, 1918; A. L. Kimball and D. E. Lovell, *ib.*, (2), **30**. 948, 1927; H. B. de Vore and W. P. Davey, *ib.*, (2), **31**. 160, 1928; W. E. W. Millington and F. C. Thompson, *Nature,* **117**. 720, 1926; R. Tajime, *Nagoka's Anniv. Vol.*, 413, 1925; *Japan. Journ. Phys.*, **4**. 23, 1925; K. Iokibe and S. Sakai, *Proc. Phys. Math. Soc. Japan,* (3), **2**. 93, 1920; *Science Rep. Tohoku Univ.*, **10**. 1, 1921; *Phil. Mag.*, (6), **42**. 397, 1921; E. Edwards, I. Bowen and S. Alty, *ib.*, (7), **2**. 321, 1926; G. Subrahmaniam, *ib.*, (7), **1**. 1074, 1926; M. Grube, *Zeit. Ges. Giessereipr.*, **47**. 173, 1926; *Chim. Ind.*, **18**. 68, 1927; F. von Göler and G. Sachs, *Zeit. Metallkunde,* **19**. 410, 1927; C. H. Jones, *Chem. Met. Engg.*, **22**. 9, 1920; P. W. Bridgman, *Proc. Amer. Acad.*, **64**. 39, 1929; J. C. Slater, *Phys. Rev.*, (2), **36**. 57, 1930; J. Pintsch, *German Pat., D.R.P.* 291994, 1914; H. Schönborn, *Zeit. Physik,* **8**. 377, 1922; S. J. Wright, *Proc. Roy. Soc.*, **126**. A, 613, 1930; W. G. Bugers, *Zeit. Physik,* **58**. 11, 1929; T. Fujiwara, *Mem. Coll. Kyoto,* **13**. 109, 149, 1930; R. F. Mehl, *Journ. Amer. Chem. Soc.*, **52**. 534, 1930.

[3] W. Widder, *Phys. Zeit.*, **26**. 618, 1925; C. G. Fink, *Trans. Amer. Electrochem. Soc.*, **17**. 229, 1910; *Met. Chem. Engg.*, **8**. 341, 1910; *Chem. News,* **104**. 34, 1911; *Journ. Ind. Eng. Chem.*, **5**. 8, 1913; D. W. Berlin, *Journ. Iron Steel Inst.—Carnegie Mem.*, **13**. 167, 1924; I. Langmuir, *Gen. Elect. Rev.*, **19**. 211, 1916; *Phys. Rev.*, (2), **7**. 302, 1916; A. G. Worthing, *ib.*, (2), **4**. 535, 1914; (2), **10**. 638, 1917; *Bull. Nela Research Lab.*, **1**. 338, 1922; *Journ. Franklin Inst.*, **181**. 857, 1916; F. S. Goucher, *Phil. Mag.*, (6), **48**. 229, 1924; J. Disch, *Zeit. Physik,* **5**. 173, 1921; P. Hidnert and W. T. Sweeney, *Thermal Expansion of Tungsten,* Washington, 1925; *Scient. Papers Bur. Standards,* **20**. 483, 1925; *Phys. Rev.*, (2), **27**. 519, 1926; H. L. Dodge, *ib.*, (2), **11**. 311, 1918; C. J. Smithells, *Tungsten,* London, 54, 115, 1926; K. Becker, *Naturwiss.*, **14**. 1036, 1926; *Zeit. Physik,* **40**. 37, 1926; W. D. Coolidge, *Trans. Amer. Inst. Elect. Eng.*, **31**. 870, 1912; S. Weber, *Ann. Physik,* (4), **54**. 165, 1917; T. Barratt and R. M. Winter, *ib.*, (4), **77**. 1, 1925; *Proc. Phys. Soc.*, **26**. 347, 1914; C. Zwikker and G. Schmidt, *Physica,* **8**. 329, 1928; C. Zwikker, *Arch. Néerl.*, (3), **9**. 207, 1925; *Versl. Akad. Amsterdam,* **34**. 468, 1925; **36**. 856, 1927; *Proc. Acad. Amsterdam,* **28**. 498, 1925; H. L. Dodge, *Phys. Rev.*, (2), **11**. 311, 1918; E. Grüneisen and E. Goens, *Zeit. Physik,* **44**. 615, 1927.

[4] H. V. Regnault, *Ann. Chim. Phys.*, (2), **73**. 48, 1840; (3), **63**. 23, 1861; *Bull. Soc. Chim.*, (1), **4**. 83, 1862; P. Debye, *Phys. Zeit.*, **18**. 483, 1917; J. Dewar, *Proc. Roy. Soc.*, **89**. A, 158, 1913; P. Nordmeyer and A. L. Bernoulli, *Ber. deut. phys. Ges.*, **5**. 175, 1907; *Verh. deut. phys. Ges.*, **9**. 175, 1907; M. von Pirani, *ib.*, **14**. 1037, 1912; A. W. Grodspeed and E. F. Smith, *Zeit. anorg. Chem.*, **8**. 207, 1895; L. Weiss, *ib.*, **65**. 334, 1910; J. Maydel, *ib.*, **178**. 113, 1929; **186**. 289, 1930; W. Geiss and J. A. M. van Liempt, *ib.*, **171**. 317, 1928; H. Mache, *Sitzber. Akad. Wien,* **106**. 590, 1897; E. Defacqz and M. Guichard, *Ann. Chim. Phys.*, (7), **24**. 139, 1901; K. K. Smith and L. I. Bockstahler, *Proc. Nat. Acad.*, **10**. 386, 1924; L. I. Bockstahler, *Phys. Rev.*, (2), **25**. 677, 1925; K. K. Smith and P. W. Bigler, *ib.*, (2), **19**. 268, 1922; P. F. Gaehr, *ib.*, (2), **12**. 396, 1918; (2), **20**. 375, 1922; A. G. Worthing, *ib.*, (2), **12**. 199, 1918; *Bull. Nela Research Lab.*, **1**. 349, 1922; *Franklin Inst.*, **185**. 707, 1918; F. Lange, *Zeit. phys. Chem.* **110**. 343, 1924; F. M. Jäger and E. Rosenbohm, *Versl. Akad. Amsterdam,* **30**. 763, 1927; *Proc. Akad. Amsterdam,* **30**. 1069, 1927; **33**. 457, 1930; *Rec. Trav. Chim. Pays-Bas,* **47**. 513, 1928; W. M. Latimer, *Journ. Amer. Chem. Soc.*, **44**. 2136, 1922; G. N. Lewis, G. E. Gibson and W. M. Latimer, *ib.*, **44**. 1008, 1922; E. D. Eastman, *ib.*, **45**. 80, 1923; E. D. Eastman, A. M. Williams and T. F. Young, *ib.*, **46**. 1184, 1924; E. Grüneisen, *Ann. Physik,* (4), **26**. 211, 1908; A. Magnus and H. Danz, *ib.*, (4), **81**. 407, 1926; A. Magnus and H. Holzmann, *ib.*, (4), **35**. 585, 1929; (5), **3**. 585, 1929; H. Holzmann, *Untersuchungen über die spezifischen Wärmen von Tantal, Wolfram und Beryllium zwischen* 100°–900° *C.*, Leipzig, 1929; H. Danz, *Die spezifische Wärme von Wolfram, Bor, Borstickstoff und Berylliumoxyd,* Leipzig, 1926; F. Wüst, A. Meuthen and R. Durrer, *Ver. deut. Ing. Forschungsarb.*, 204, 1918; H. A. Jones and I. Langmuir, *Gen. Elect. Rev.*, **30**. 310, 344, 1927; H. A. Jones, I. Langmuir and G. M. J. McKay, *Phys. Rev.*, (2), **30**. 201, 1927; O. M. Corbino, *Atti Accad. Lincei,* (5), **21**. 1, 181, 346, 1912; *Phys. Zeit.*, **11**. 413, 1910; **13**. 375, 1912; H. Hunkel, *ib.*, **12**. 252, 1923; C. Zwikker, *Zeit. Physik,* **52**. 668, 1929; C. Zwikker and G. Schmidt, *Physica,* **8**. 329, 1928.

[5] C. W. Siemens and A. K. Huntington, *Chem. News,* **46**. 163, 1882; H. Moissan, *Ann. Chim. Phys.*, (7), **8**. 570, 1896; *Le four électrique,* Paris, 229, 1897; London, 159, 1904; *Compt. Rend.*, **73**. 13, 1872; **116**. 1225, 1893; **123**. 13, 1896; L. Weiss, *Zeit. anorg. Chem.*, **65**. 334, 1910; E. Tiede and E. Birnbräuer, *ib.*, **87**. 129, 1914; W. Herz, *ib.*, **94**. 8, 1916; J. A. M. van Liempt, *ib.*, **114**. 105, 1920; M. von Pirani and A. R. Meyer, *Ber. deut. phys. Ges.*, **14**. 426, 1912; M. von Pirani, *ib.*, **14**. 426, 1912; *Verh. deut. phys. Ges.*, **12**. 301, 1910; M. von Pirani and H. Alterthum, *Zeit. Elektrochem.*, **29**. 5, 1923; E. Lax and M. Pirani, *Zeit. Physik,* **22**. 275, 1924; Allgemeine Elektrizitäts-Gesellschaft, *German Pat., D.R.P.* 201567, 1907; M. Arndt, *ib.*, 235135, 1909; O. Ruff and O. Goecke, *Ber.*, **43**. 1564, 1910; O. Ruff, *Zeit. angew. Chem.*, **24**. 2244, 1911; **25**. 1894, 1912; H. von Wartenberg, *ib.*, **24**. 2243, 1911; *Ber.*, **40**. 3287, 1907; C. W. Waidner and G. K. Burgess, *Bull. Bur. Standards,* **2**. 319, 1906; *L'Electricien,* (2), **34**. 13, 1907; G. K. Burgess, *Journ. Washington Acad.*, **1**. 16, 1912; F. Henning and W. Heuse, *Zeit. Physik,* **16**. 63, 1923; B. Bruzs, *Journ. Phys. Chem.*, **31**. 681, 1927; G. R. Fonda, *Phys. Rev.*, (2), **21**. 343, 1923; (2), **31**. 260, 1928; A. G. Worthing, *ib.*, (2), **7**. 497, 1916; (2), **19**. 383, 1922; (2), **25**. 846, 1925; *Zeit. Physik,* **22**. 9, 1924; *Journ. Franklin Inst.*, **181**. 417, 1916; A. G. Worthing and W. C. Baker, *ib.*, **191**. 833, 835, 1921; A. G. Worthing and W. E. Forsythe, *Phys. Rev.*, (2), **18**. 144, 1921; *Astrophys. Journ.*, **61**. 146, 1925; I. Langmuir, *Phys. Zeit.*, **14**. 1273, 1913; *Brit. Pat. No.* 10918,

1913 ; *Phys. Rev.*, (2), **2**. 329, 1912 ; (2), **4**. 377, 1914 ; (2), **6**. 138, 1915 ; *Journ. Franklin Inst.*, **180**. 490, 1915 ; *Journ. Amer. Chem. Soc.*, **35**. 931, 1913 ; H. A. Jones and I. Langmuir, *Gen. Elect. Rev.*, **30**. 310, 344, 1927 ; H. A. Jones, I. Langmuir and G. M. J. MacKay, *Phys. Rev.*, (2), **30**. 201, 1927 ; H. A. Jones, *ib.*, (2), **28**. 202, 1926 ; M. L. Phillips, *ib.*, (2), **32**. 832, 1928 ; M. R. Andrews, *ib.*, (2), **33**. 454, 1929 ; W. R. Mott, *Trans. Amer. Electrochem. Soc.*, **34**. 255, 1918 ; W. E. Forsythe, *A Determination of the Melting Points of Tantalum and Tungsten*, Philadelphia, 1911 ; *Phys. Rev.*, (2), **19**. 436, 1922 ; *Astrophys. Journ.*, **34**. 352, 1911 ; C. G. Fink, *Trans. Amer. Electrochem. Soc.*, **22**. 499, 1912 ; *Met. Chem. Engg.*, **8**. 341, 1910 ; *Chem. News*, **104**. 34, 1911 ; M. Delépine and L. A. Hallopeau, *Compt. Rend.*, **129**. 600, 1899 ; M. Delépine, *ib.*, **131**. 184, 1900 ; *Bull. Soc. Chim.*, (3), **23**. 675, 1900 ; G. N. Lewis, G. E. Gibson and W. M. Latimer, *Journ. Amer. Chem. Soc.*, **44**. 1008, 1922 ; E. D. Eastman, *ib.*, **45**. 80, 1923 ; W. H. Rodebush, *ib.*, **45**. 997, 1923 ; J. E. Moose and S. W. Parr, *ib.*, **46**. 2656, 1924 ; W. M. Latimer, *ib.*, **34**. 2136, 1922 ; R. C. Tolman, *ib.*, **42**. 1185, 1920 ; E. D. Eastman, A. M. Williams and T. F. Young, *ib.*, **46**. 1185, 1924 ; F. S. Mortimer, *ib.*, **44**. 1429, 1922 ; P. Winternitz, *Phys. Zeit.*, **15**. 397, 1914 ; W. G. Mixter, *Amer. Journ. Science*, (4), **26**. 125, 1908 ; G. P. Luckey, *Electrician*, **77**. 947, 1916 ; *Journ. Franklin Inst.*, **182**. 407, 1916 ; *Phys. Rev.*, (2), **9**. 129, 1917 ; *Bull. Nela Research Lab.*, **1**. 341, 1922 ; C. Zwikker, *Arch. Néerl.*, (3), **9**. 207, 1925 ; *Versl. Akad. Amsterdam*, **34**. 468, 1925 ; **35**. 336, 1926 ; *Proc. Acad. Amsterdam*, **28**. 498, 1925 ; **29**. 792, 1926 ; **30**. 853, 1927 ; R. Davis and K. S. Gibson, *Phys. Rev.*, (2), **29**. 916, 1927 ; L. P. Sieg, *ib.*, (2), **25**. 251, 1925 ; J. A. M. van Liempt, *Zeit. anorg. Chem.*, **129**. 263, 1923 ; **189**. 287, 1930 ; W. Herz, *ib.*, **177**. 116, 1928 ; **180**. 284, 1929 ; F. Koref and H. Wolff, *Zeit. Elektrochem.*, **28**. 477, 1922 ; F. Wolfers, *Radioélectricité*, **4**. 10, 22, 1923 ; L. Hamburger, G. Holst, D. Lely and E. Oosterhuis, *Proc. Acad. Amsterdam*, **21**. 1078, 1919 ; E. Oosterhuis, *Verh. Med. Nat. en Geneesk. Congres*, **16**. 101, 1917 ; S. Weber, *Danske Selsk. Medd.*, **3**. 3, 1920 ; P. Woog, *Bull. Soc. Chim.*, (4), **39**. 1708, 1926 ; H. Hunkel, *Phys. Zeit.*, **24**. 252, 1923 ; F. Simon, *Zeit. phys. Chem.*, **110**. 572, 1924 ; H. C. von Alphen, *Ann. Physik*, (4), **85**. 1058, 1928 ; R. Kleeman, *Journ. Phys. Chem.*, **31**. 1669, 1927 ; H. Alterthum, *Zeit. tech. Phys.*, **9**. 285, 1928 ; F. J. Wilkins, *Nature*, **125**. 236, 1930.

[6] E. Lax and M. Pirani, *Zeit. Physik*, **22**. 275, 1924 ; F. E. Dix and L. H. Rowse, *Journ. Amer. Optical Soc.*, **14**. 304, 1927 ; H. von Wartenberg, *Verh. deut. phys. Ges.*, **12**. 105, 129, 1910 ; G. Holst, E. Lax, E. Oosterhuis and M. Pirini, *Zeit. tech. Phys.*, **9**. 186, 1928 ; A. Grau, *Elekt. Masch.*, **25**. 295, 1907 ; W. W. Coblentz, *Journ. Franklin Inst.*, **170**. 169, 1910 ; *Bull. Bur. Standards*, **5**. 372, 1909 ; *Supplementary Investigations of Infra red Spectra*, Washington, 92, 1908 ; *Phys. Rev.*, (1), **30**. 645, 1910 ; G. Jaffé, *Ann. Physik*, (4), **45**. 1217, 1915 ; W. Geiss, *ib.*, (4), **79**. 85, 1926 ; H. C. von Alphen, *ib.*, (4), **85**, 1058, 1928 ; E. Furthmann, *Ueber der Gesambstrahlung fester Körper*, Düsseldorf, 1928 ; N. A. de Bruyne, *Proc. Cambridge Phil. Soc.*, **25**. 347, 1929 ; F. K. Moss and M. Luckiesh, *Journ. Franklin Inst.*, **205**. 565, 1928 ; J. T. Littleton, *Phys. Rev.*, (1), **35**. 306, 1912 ; I. Langmuir, *ib.*, (2), **6**. 138, 1916 ; *Phys. Zeit.*, **14**. 1273, 1913 ; *Journ. Amer. Chem. Soc.*, **35**. 105, 931, 1913 ; I. Langmuir and G. M. J. Mackay, *Zeit. Elektrochem.*, **20**. 498, 1914 ; W. E. Forsythe and F. Christison, *Gen. Elect. Rev.*, **22**. 662, 1929 ; W. E. Forsythe, *Phys. Rev.*, (2), **19**. 436, 1922 ; A. G. Worthing and W. E. Forsythe, *Astrophys. Journ.*, **61**. 146, 1925 ; *Journ. Franklin Inst.*, **199**. 261, 1925 ; *Phys. Rev.*, (2), **18**. 144, 1921 ; A. G. Worthing, *ib.*, (2), **7**. 497, 1916 ; (2), **10**. 377, 1917 ; *Journ. Amer. Opt. Soc.*, **13**. 635, 1926 ; *Zeit. Physik*, **22**. 9, 1924 ; *Proc. Amer. Phys. Soc.*, **35**. 76, 1913 ; *Journ. Amer. Opt. Soc.*, **13**. 635, 1926 ; *Elect. Rev.*, **62**. 706, 1913 ; H. A. Jones and I. Langmuir, *Gen. Elect. Rev.*, **30**. 310, 344, 1927 ; *Journ. Franklin Inst.*, **181**, 417, 857, 1916 ; E. O. Hulbert, *ib.*, **182**. 695, 1916 ; E. P. Hyde, F. E. Cady and W. E. Forsythe, *ib.*, **131**. 418, 420, 1916 ; W. E. Forsythe and E. M. Watson, *ib.*, **206**. 535, 1928 ; H. B. Dorgelo, *Zeit. Physik*, **36**. 467, 1926 ; A. L. Hellgott, *ib.*, **49**. 555, 1928 ; C. J. Smithells, *Tungsten*, London, 103, 1926 ; B. P. Dudding and C. J. Smithells, *Beama*, **13**. 221, 1923 ; C. Zwikker, *Arch. Néerl.*, (3), **9**. 207, 1925 ; *Versl. Akad. Amsterdam*, **34**. 468, 1925 ; **36**. 856, 1927 ; *Proc. Acad. Amsterdam*, **28**. 498, 1925 ; R. E. Nyswander, *Phys. Rev.*, (1), **28**. 438, 1909 ; W. Weniger and A. H. Pfund, *ib.*, (2), **14**. 427, 1919 ; H. A. James, *ib.*, (2), **28**. 202, 1926 ; B. E. Shackelford, *ib.*, (2), **8**. 470, 1916 ; A. H. Taylor, *Journ. Franklin Inst.*, **203**. 716, 1927 ; F. Henning, *Jahrb. Rad. Elektron.*, **17**. 30, 1920 ; B. T. Barnes, *Journ. Phys. Chem.*, **33**. 688, 1929 ; *Phys. Rev.*, (2), **36**. 1468, 1930 ; R. Hamer, *ib.*, (2), **26**. 285, 1925 ; G. Ribaud, *Journ. Phys. Rad.*, (7), **1**. 176, 1930.

[7] O. W. Richardson, *The Emission of Electrons under the Influence of Chemical Action*, London, 1921 ; *Phys. Zeit.*, **14**. 793, 1913 ; *Phil. Mag.*, (6), **26**. 345, 1913 ; O. W. Richardson and F. S. Robertson, *ib.*, (6), **43**. 557, 1922 ; N. A. de Bruyne, *ib.*, (7), **5**. 574, 1928 ; S. C. Roy, *ib.*, (6), **47**. 561, 1924 ; *Proc. Roy. Soc.*, **112**. A, 599, 1926 ; R. H. Fowler, *ib.*, **117**. A, 549, 1928 ; R. S. Bartlett, *ib.*, **121**. A, 456, 1928 ; N. A. de Bruyne, *ib.*, **120**. A, 423, 1928 ; *Proc. Cambridge Phil. Soc.*, **25**. 347, 1929 ; L. A. du Bridge, *Proc. Nat. Acad.*, **14**. 788, 1928 ; A. H. Warner, *ib.*, **13**. 56, 1927 ; E. H. Hall, *ib.*, **15**. 126, 1929 ; H. Klumb, *Ueber den Einfluss der Gasbeladung auf lichtelektrische Empfindlichkeit der Metalle*, Berlin, 1928 ; P. A. Ross, *Journ. Amer. Opt. Soc.*, **16**. 375, 1928 ; S. Dushman, H. N. Rowe, J. Ewald and C. A. Kidner, *Phys. Rev.*, (2), **21**. 207, 1923 ; (2), **25**. 338, 1925 ; S. Dushman and J. W. Ewald, *Gen. Elect. Rev.*, **26**. 154, 1923 ; *Phys. Rev.*, (2), **20**. 109, 1922 ; (2), **29**. 857, 1927 ; S. Dushman, D. Dennison and N. B. Reynolds, *ib.*, (2), **29**. 903, 1927 ; I. Langmuir, *Phys. Zeit.*, **15**. 348, 516, 1914 ; *Phys. Rev.*, (2), **20**. 107, 1922 ; (2), **22**. 357, 1923 ; R. J. Piersol, *ib.*, (2), **31**. 441, 1928 ; R. A. Millikan and C. C. Lauritsen, *ib.*, (2), **33**. 598, 1929 ; L. P. Smith, *ib.*, (2), **33**. 1082, 1929 ; H. L. van Velzer and W. R. Ham, *ib.*, (2), **33**. 1083, 1929 ; W. H. Crew, *ib.*, (2), **28**. 1265, 1926 ; C. del Rosario, *ib.*, (2), **28**. 768, 1926 ;

H. E. Farnsworth, *ib.*, (2), **25**. 41, 1925 ; W. R. Ham and M. W. White, *ib.*, (2), **23**. 777, 1924 ; (2), **27**. 111, 510, 1926 ; L. H. Germer, *ib.*, (2), **25**. 795, 1925 ; C. C. Lauritsen and S. S. Mackeown, *ib.*, (2), **32**. 326, 1928 ; A. G. Worthing, *ib.*, (2), **22**. 9, 1924 ; *Journ. Amer. Opt. Soc.*, **13**. 635, 1926 ; *Journ. Franklin Inst.*, **191**. 837, 1921 ; F. E. Colpitts, *ib.*, **206**. 489, 1928 ; H. E. Ives, *ib.*, **201**. 47, 1926 ; K. H. Kingdon, *Phys. Rev.*, (2), **24**. 510, 1924 ; J. M. Eglin, *ib.*, (2), **31**. 1127, 1928 ; I. Langmuir and K. H. Kingdon, *ib.*, (2), **22**. 148, 1923 ; *Proc. Roy. Soc.*, **107**. A, 61, 1925 ; I. Langmuir, *Journ. Ind. Eng. Chem.*, **22**. 390, 1930 ; I. Langmuir and D. S. Villars, *Journ. Amer. Chem. Soc.*, **53**. 486, 1931 ; K. K. Smith, *Proc. Phys. Soc.*, **38**. 1, 1925 ; *Phil. Mag.*, (6), **29**. 802, 1915 ; H. H. Lester, *ib.*, (6), **31**. 197, 1916 ; P. K. Mitra, *ib.*, (7), **5**. 67, 1928 ; W. Hüttemann, *Ann. Physik*, (4), **52**. 816, 1917 ; J. A. Becker, *ib.*, (2), **27**. 112, 811, 1926 ; H. Hunkel, *Phys. Zeit.*, **24**. 252, 1923 ; R. Hamer, *Journ. Amer. Opt. Soc.*, **9**. 251, 1924 ; A. C. Davies and R. N. Moss, *Phil. Mag.*, (7), **5**. 989, 1928 ; C. J. Smithells, *Journ. Chem. Soc.*, **121**. 2236, 1922 ; *Tungsten*, London, 112, 1926 ; A. S. Cachemaille, *Brit. Pat. No.* 240560, 240909, 1924 ; British Thomson-Houston Co., 215348, 1924 ; C. Zwikker, *Arch. Néerl.*, (3), **9**. 207, 1925 ; *Versl. Akad. Amsterdam*, **34**. 468, 1925 ; **35**. 336, 1926 ; *Proc. Acad. Amsterdam*, **28**. 498, 1925 ; **29**. 792, 1926 ; **30**. 853, 1927 ; H. E. Krefft, *Ann. Phys.*, (4), **84**. 639, 1927 ; *Phys. Rev.*, (2), **29**. 908, 1927 ; (2), **31**. 199, 1928 ; A. T. Waterman, *ib.*, (2), **24**. 366, 1924 ; J. A. M. van Liempt, *Nature*, **115**. 194, 1925 ; H. Jones and R. Whiddington, *Proc. Leeds Lit. Phil. Soc.*, **1**. 160, 1927 ; L. I. Bockstahler, *Phys. Rev.*, (2), **31**. 303, 1928 ; J. A. Becker and D. W. Mueller, *ib.*, (2), **31**. 308, 431, 1928 ; H. Nukiyama and H. Horikawa, *Tech. Rep. Tohoku Univ.*, **7**. 49, 1927 ; E. Lorenz, *Proc. Nat. Acad.*, **14**. 582, 1928 ; F. Rother and E. Münder, *Phys. Zeit.*, **30**. 65, 1929 ; T. E. Stern, B. S. Gossling and R. H. Fowler, *Proc. Roy. Soc.*, **124**. A, 699, 1929 ; S. Kalandyk, *Journ. Phys. Rad.*, (6), **10**. 337, 1929 ; W. E. Forsythe and E. M. Watson, *Journ. Franklin Inst.*, **206**. 535, 1928 ; M. Pirani and H. Schönborn, *Naturwiss.*, **15**. 767, 1927 ; E. Meyer, *Ueber die Elektronen und positive Ionemission von Wolfram-, Molybdan-, und Tantalglühfäden in Kaliumdampf*, Berlin, 1930 ; *Ann. Physik*, (5), **4**. 557, 1930 ; E. Spiller, *Zeit. Physik*, **64**. 39, 1930 ; G. P. Thomson, *Proc. Roy. Soc.*, **128**. A, 649, 1930 ; G. E. Berger, *Phys. Rev.*, (2), **34**. 1566, 1929 ; K. Sixtus, *Ann. Physik*, (5), **3**. 1017, 1929 ; W. G. Burgers and J. A. M. van Liempt, *Zeit. anorg. Chem.*, **193**. 144, 1930 ; W. B. Nottingham, *Phys. Rev.*, (2), **36**. 376, 1930 ; W. H. Brattain, *ib.*, (2), **35**. 1431, 1930 ; H. N. Kozanowsky, *ib.*, (2), **35**. 1430, 1930 ; C. C. van Voorhis, *ib.*, (2), **29**. 318, 1927 ; C. C. van Voorhis and K. T. Compton, *ib.*, (2), **36**. 1435, 1930 ; *Proc. Nat. Acad.*, **13**. 336, 1927.

[8] W. A. Jenkins, *Phil. Mag.*, (6), **47**. 1025, 1924 ; P. K. Mitra, *ib.*, (6), **5**. 67, 1928 ; R. H. Whiddington, *ib.*, (6), **43**. 1116, 1922 ; J. F. Congdon, *ib.*, (4), **47**. 458, 1924 ; C. Kenty and L. A. Turner, *Nature*, **120**. 332, 1927 ; *Phys. Rev.*, (2), **29**. 914, 1927 ; R. L. Kenworthy, *ib.*, (2), **27**. 112, 1926 ; O. Stuhlman, *ib.*, (2), **23**. 296, 1924 ; A. G. Worthing, *ib.*, (2), **22**. 9, 1924 ; *Journ. Amer. Opt. Soc.*, **13**. 635, 1926 ; *Journ. Franklin Inst.*, **191**. 837, 1921 ; S. C. Roy, *Proc. Roy. Soc.*, **112**. A, 599, 1926 ; H. Klumb, *Zeit. Physik*, **47**. 652, 1928 ; A. H. Warner, *Proc. Nat. Acad.*, **13**. 56, 1927 ; W. de Groot, *Physica*, **5**. 121, 1925 ; T. H. Harrison, *Proc. Phys. Soc.*, **38**. 214, 1926 ; R. L. Petry, *Phys. Rev.*, (2), **28**. 362, 1926 ; C. Davison and L. H. Germer, *ib.*, (2), **19**. 439, 1922 ; (2), **20**. 300, 1922 ; (2), **30**. 634, 1927 ; H. E. Farnsworth, *ib.*, (2), **25**. 41, 1925 ; R. Hamer, *ib.*, (2), **20**. 198, 1922 ; C. C. Lauritsen and S. S. Mackeown, *ib.*, (2), **32**. 326, 1928 ; L. P. Smith, *ib.*, (2), **33**. 279, 1929 ; (2), **34**. 1496, 1929 ; (2), **35**. 381, 1930 ; A. C. Davies and R. N. Moss, *Phil. Mag.*, (7), **5**. 989, 1928 ; M. Pirani and H. Schönborn, *Naturwiss.*, **15**. 767, 1927 ; H. B. Wahlin, *Nature*, **123**. 912, 1929 ; *Phys. Rev.*, (2), **35**. 653, 1930 ; E. T. S. Appleyard, *Proc. Roy. Soc.*, **128**. A, 330, 1930 ; E. Meyer, *Ann. Physik*, (5), **4**. 357, 1930 ; *Ueber die Elektronen- und positive Ionemission von Wolfram-, Molybdan-, und Tantalglühfäden in Kaliumdampf*, Berlin, 1930 ; N. B. Reynolds, *Phys. Rev.*, (2), **35**. 158, 1930 ; S. Kalandyk, *Journ. Phys. Rad.*, (6), **10**. 337, 1929.

[9] W. A. Miller, *Phil. Trans.*, **152**. 861, 1862 ; R. Thalén, *Om spectralanalys*, Upsala, 1866 ; *Nova Acta Upsala*, (3), **6**. 9, 1868 ; *Ann. Chim. Phys.*, (4), **18**. 262, 1869 ; J. N. Lockyer, *Proc. Roy. Soc.*, **43**. 117, 1887 ; *Phil. Trans.*, **173**. 561, 1881 ; V. Schumann, *Phot. Rund.*, **41**. 71, 1890 ; E. Demarçay, *Spectres électriques*, Paris, 1895 ; F. Exner and E. Haschek, *Die Spectren der Elemente bei normalen Druck*, Leipzig, 1912 ; *Wellenlängentabellen für spectralanalytische Untersuchungen auf Grund der ultravioletten Funkenspectren der Elemente*, Leipzig, 1902 ; *Wellenlängentabellen für spectralanalytische Untersuchungen auf Grund der ultravioletten Bogenspectren der Elemente*, Leipzig, 1904 ; *Sitzber. Akad. Wien*, **104**. 909, 1895 ; **105**. 389, 1896 ; **106**. 36, 1897 ; J. M. Eder and E. Valenta, *ib.*, **118**. 1077, 1909 ; **119**. 519, 1910 ; *Atlas typischer Spectren*, Wien, 1911 ; H. Kayser, *Handbuch der Spectroscopie*, Leipzig, **6**. 787, 1912 ; H. A. Rowland, *Preliminary Table of Solar Spectrum Wave-lengths*, Chicago, 1898 ; A. Hagenbach and H. Konen, *Atlas der Emissionsspectra*, Jena, 1905 ; O. Lohse, *Pub. Astrophys. Obs. Potsdam*, **12**. 109, 1902 ; W. J. Humphreys, *Astrophys. Journ.*, **6**. 169, 1897 ; **26**. 18, 1907 ; P. G. Nutting, *ib.*, **23**. 64, 1906 ; C. R. Hasselberg, *Svenska Akad. Handl.*, **38**. 5, 1904 ; F. E. Baxandall, *Researches on the Chemical Origin of various Lines in Solar and Stellar Spectra*, London, 1910 ; R. Jack, *Zeemaneffect an Wolfram und Molybdän*, Göttingen, 1908 ; *Ann. Physik*, (4), **28**. 1032, 1909 ; *Proc. Roy. Soc. Edin.*, **29**. 75, 1909 ; A. G. G. Leonard, *Proc. Roy. Soc. Dublin*, (3), **11**. 270, 1908 ; J. H. Pollok, *ib.*, (2), **10**. 185, 1907 ; J. Stock, *Phys. Zeit.*, **10**. 694, 1909 ; H. W. Vogel, *Praktische Spektralanalyse irdischer Stoffe*, Berlin, 1889 ; P. Zeeman, *Arch. Néerl.*, (3), **13**. 260, 1908 ; G. P. Luckey, *Phys. Rev.*, (2), **9**. 129, 1917 ; O. Laporte, *Naturwiss.*, **13**. 627, 1925 ; *Phys. Rev.*, (2), **25**. 886, 1925 ; E. O. Hulbert, *ib.*, (2), **24**. 129, 1924 ; (2), **25**. 888, 1925 ; A. G. Worthing and R. Rudy, *ib.*, (2), **23**. 767, 1924 ;

C. Horner, *Chem. News*, **29.** 66, 1874 ; A. W. Hull, *Gen. Elect. Rev.*, **19.** 603, 1916 ; J. Formanek, *Die qualitative Spektralanalyse anorganischer und organischer Körper*, Berlin, 155, 1905 ; A. de Gramont, *Compt. Rend.*, **171.** 1106, 1916 ; M. Bayen, *ib.*, **180.** 57, 1925 ; L. and E. Bloch, *ib.*, **180.** 133, 1925 ; *Journ. Phys. Rad.*, **6.** 105, 1925 ; C. C. Kiess and W. F. Meggers, *Bull. Bur. Standards*, **16.** 51, 1920 ; M. Belke, *Das Bogenspektrum des Wolframs*, Leipzig, 1917 ; *Zeit. wiss. Photochem.*, **17.** 132, 145, 1917 ; H. B. Lemon, *Nature*, **115.** 802, 1925 ; H. B. Dorgelo, *Zeit. Physik*, **36.** 467, 1926 ; H. Beining, *ib.*, **42.** 146, 1927 ; W. H. Fulweiler and J. Barnes, *Journ. Franklin Inst.*, **194.** 83, 1922 ; M. Luckiesh, *ib.*, **185.** 552, 1918 ; *Bull. Nela Research Lab.*, **1.** 492, 1922 ; E. Paulson, *Beiträge zur Kenntnis der Linenspectren*, Lund, 1914 ; *Arsschrift Lund. Univ.*, (2), **10.** 12, 1914 ; A. Sellerio, *Nuovo Cimento*, (6), **25.** 69, 1923 ; C. Porlezza and A. Donati, *Ann. Chim. Applicata*, **17.** 14, 1927 ; J. C. McLennan, A. B. McLay and H. G. Smith, *Proc. Roy. Soc.*, **112.** A, 76, 1926 ; S. Smith, *Proc. Nat. Acad.*, **10.** 4, 1924 ; *Astrophys. Journ.*, **61.** 186, 1925 ; E. J. Allin and H. J. C. Ireton, *Trans. Roy. Soc. Canada*, (3), **21.** 127, 1927 ; E. J. Allin, *ib.*, (3), **21.** 231, 1927 ; T. Aden, *Die Aenderungen der Absorptionsspektren in sichtbaren und ultravioletten Gebiet bei Aggregationen in Lösungen schwacher anorganischer Säuren und ihrer Salze*, Göttingen, 1929 ; W. E. Forsythe and F. Christison, *Journ. Amer. Opt. Soc.*, **20.** 396, 1930 ; W. E. Forsythe and M. R. Easley, *Phys. Rev.*, (2), **36.** 150, 1930.

[10] P. Günther, *Naturwiss.*, **14.** 1113, 1926 ; M. de Broglie, *Compt. Rend.*, **157.** 1413, 1913 ; **158.** 117, 1913 ; **162.** 596, 1916 ; **169.** 962, 1919 ; **170.** 248, 1053, 1920 ; A. Dauvillier, *ib.*, **72.** 915, 1921 ; **173.** 647, 1921 ; **182.** 927, 1926 ; **183.** 193, 1926 ; V. Posejpal, *ib.*, **182.** 272, 767, 1926 ; P. Auger, *ib.*, **186.** 785, 1928 ; R. Ledoux-Lebard and A. Dauvillier, *ib.*, **163.** 574, 1917 ; **164.** 687, 1917 ; *Le physique des rayons-X*, Paris, 1921 ; G. Réchou, *Compt. Rend.*, **180.** 1107, 1925 ; J. Herweg, *Verh. deut. phys. Ges.*, **16.** 73, 1914 ; W. Ehrenberg and H. Mark, *Zeit. Physik*, **42.** 807, 1927 ; W. Ehrenberg and G. vom Susich, *ib.*, **42.** 823, 1927 ; J. Barnes, *Phil. Mag.*, (6), **30.** 368, 1915 ; H. G. J. Moseley, *ib.*, (6), **27.** 703, 1914 ; R. Whiddington, *ib.*, (6), **43.** 116, 1922 ; C. D. Niven, *ib.*, (7), **3.** 1314, 1927 ; M. Siegbahn, *ib.*, (6), **38.** 639, 1919 ; *Zeit. Physik*, **50.** 443, 1928 ; *Jahrb. Rad. Elektron.*, **18.** 240, 1921 ; *Phys. Zeit.*, **20.** 533, 1919 ; A. Jönsson, *ib.*, **43.** 845, 1927 ; M. Siegbahn and E. Friman, *Ann. Physik*, (4), **49.** 616, 1916 ; *Zeit. Physik*, **39.** 813, 1926 ; A. H. Compton, *Phys. Rev.*, (2), **7.** 496, 646, 1916 ; J. M. Cork, *ib.*, (2), **21.** 326, 1923 ; (2), **25.** 197, 1925 ; W. S. Gorton, *ib.*, (2), **7.** 203, 1916 ; W. Duane and W. Stenstrom, *ib.*, (2), **15.** 328, 1920 ; *Proc. Nat. Acad.*, **6.** 477, 1920 ; W. Duane, H. Fricke and W. Stenstrom, *ib.*, **6.** 607, 1920 ; W. Duane and T. Shimizu, *Phys. Rev.*, (2), **14.** 522, 1919 ; W. Duane and R. A. Patterson, *ib.*, (2), **16.** 526, 1920 ; *Proc. Nat. Acad.*, **6.** 509, 1920 ; A. W. Hull and M. Rice, *ib.*, **2.** 265, 1916 ; A. W. Hull, *Gen. Elect. Rev.*, **19.** 603, 1916 ; E. Dershem, *Proc. Iowa Acad.*, **23.** 191, 1916 ; *Phys. Rev.*, (2), **11.** 244, 461, 1918 ; R. V. Zumstein, *ib.*, (2), **25.** 106, 747, 1925 ; O. B. Overn, *ib.*, (2), **14.** 137, 1919 ; D. Coster, *Phil. Mag.*, (6), **43.** 1070, 1922 ; *Zeit. Physik*, **4.** 178, 1921 ; **6.** 185, 1921 ; *Phys. Rev.*, (2), **18.** 218, 1921 ; (2), **19.** 20, 1922 ; J. E. Mack and J. M. Cork, *ib.*, (2), **30.** 741, 1927 ; B. R. Stephenson and J. M. Cork, *ib.*, (2), **27.** 138, 1926 ; P. Kirkpatrick and I. Miyake, *Proc. Nat. Acad.*, **15.** 418, 1929 ; *Phys. Rev.*, (2), **33.** 268, 1929 ; E. C. Watson and J. A. van der Akker, *ib.*, (2), **34.** 347, 1929 ; F. K. Richtmyer, *ib.*, (2), **27.** 1, 1926 ; P. A. Ross, *ib.*, (2), **26.** 281, 1926 ; S. K. Allison and A. H. Armstrong, *ib.*, (2), **26.** 714, 1925 ; *Proc. Nat. Acad.*, **11.** 536, 1925 ; S. K. Allison and W. Duane, *ib.*, **11.** 25, 1925 ; M. Thoræus, *Zeit. Physik*, **26.** 396, 1924 ; E. Hjalmar, *Phys. Zeit.*, **3.** 262, 1920 ; **15.** 65, 1923 ; E. Friman, *Zeit. Physik*, **39.** 813, 1926 ; G. Wentzel, *Naturwiss.*, **10.** 369, 1922 ; A. Bouwers, *Physica*, **5.** 8, 1925 ; A. Smekal, *Sitzber. Akad. Wien*, **130.** 25, 1911 ; *Zeit. Physik*, **5.** 91, 1921 ; A. Leide, *ib.*, **39.** 686, 1926 ; C. B. Bozzani and C. T. Chu, *Journ. Franklin Inst.*, **197.** 183, 1924 ; C. T. Chu, *Phys. Rev.*, (2), **23.** 551, 1924 ; (2), **27.** 528, 1926 ; J. A. Becker, *ib.*, (2), **24.** 478, 1924 ; C. B. Crofutt, *Proc. Iowa Acad.*, **28.** 117, 1921 ; *Phys. Rev.*, (2), **23.** 105, 1924 ; (2), **24.** 9, 1924 ; (2), **27.** 243, 538, 1926 ; M. C. Magarian, *ib.*, (2), **26.** 282, 1925 ; K. T. Compton and C. H. Thomas, *ib.*, (2), **28.** 601, 1926 ; F. C. Hoyt, *ib.*, (2), **18.** 333, 1921 ; H. Purks, *ib.*, (2), **31.** 931, 1928 ; F. L. Hunt, *ib.*, (2), **30.** 227, 1927 ; H. Hirata, *Proc. Roy. Soc.*, **105.** A. 40, 1924 ; O. Stuhlman, *Journ. Elisha Mitchell Soc.*, **41.** 20, 1925 ; *Phys. Rev.*, (2), **23.** 296, 1924 ; J. S. Rogers, *Proc. Cambridge Phil. Soc.*, **21.** 430, 1923 ; B. Walter, *Zeit. Physik*, **20.** 257, 1924 ; **30.** 357, 1924 ; H. Brauns, *Zeit. wiss. Photochem.*, **25.** 325, 1898 ; W. Kerz, *Zeit. anorg. Chem.*, **117.** 116, 1928 ; J. H. van der Tuuk, *Zeit. Physik*, **44.** 737, 1927 ; A. E. van Arkel and W. G. Burgers, *ib.*, **48.** 690, 1928 ; K. C. Mazumder, *ib.*, **46.** 449, 1927 ; E. Lorenz, *ib.*, **51.** 76, 1928 ; *Proc. Nat. Acad.*, **14.** 582, 1928 ; S. Idei, *Nature*, **123.** 643, 1929 ; E. Lindberg, *Zeit. Physik*, **50.** 82, 1928 ; **54.** 632, 1929 ; H. R. Robinson and C. L. Young, *Nature*, **123.** 203, 1929 ; H. R. Robinson, *Phil. Mag.*, (6), **50.** 241, 1925 ; B. B. Ray, *ib.*, (6), **48.** 707, 1924 ; R. Nishina, *ib.*, (6), **49.** 521, 1925 ; J. Thibaud and A. Soltan, *Journ. Phys. Rad.*, (6), **8.** 484, 1927 ; U. Yoshida and S. Tanaka, *Mem. Coll. Kyoto*, **5.** 173, 1922 ; K. Molin, *Arkiv Mat. Astron. Fysik*, **21.** 1, 1929 ; R. Berthold, *Ann. Physik*, (4), **76.** 409, 1925 ; W. H. Love, *Med. Journ. Australia*, **2.** 246, 1929 ; J. Zahradnicek, *Zeit. Physik*, **60.** 712, 1930 ; A. Sandström, *ib.*, **65.** 632, 1930 ; L. Y. Faust, *Phys. Rev.*, (2), **36.** 161, 1930 ; C. Agte and K. Becker, *Zeit. tech. Phys.*, **11.** 107, 1930 ; S. Idei, *Science Rep. Tohoku Univ.*, **19.** 559, 1930.

[11] A. Bouwers, *Physica*, **8.** 5, 1925 ; T. E. Aurén, *Phil. Mag.*, (6), **33.** 471, 1917 ; R. Whiddington, *ib.*, (6), **43.** 1116, 1922 ; R. A. Houstoun, *ib.*, (7), **2.** 512, 1926 ; W. H. Rothery, *ib.*, (7), **9.** 65, 1929 ; L. M. Alexander, *ib.*, (7), **4.** 670, 1927 ; A. H. Warner, *Phys. Rev.*, (2), **32.** 326, 1928 ; (2), **33.** 815, 1929 ; F. K. Richtmyer, *ib.*, (1), **6.** 65, 1915 ; F. W. Warburton and F. K. Richtmyer, *ib.*, (2), **23.** 291, 1924 ; J. Lifschitz, *Proc. Acad. Amsterdam*, **26.** 561, 1923 ; P. A. Ross, *Proc. Nat. Acad.*, **11.** 567, 1925 ; G. Hagen, *Ann. Physik*, (4), **78.** 407, 1925 ; F. Kirchner, *ib.*, (4), **78.** 421,

1925; D. Nasledoff and P. Sharavsky, *Phys. Zeit.*, **28**. 549, 1927; C. J. Smithells and H. P. Rooksby, *Journ. Chem. Soc.*, 1882, 1927; A. Jönsson, *Zeit. Physik*, **36**. 426, 1926; J. H. van der Tuuk, *ib.*, **44**. 737, 1927; S. J. M. Allen, *Phys. Rev.*, (2), **24**. 1, 1924; (2), **27**. 267, 1926; (2), **28**. 907, 1926; A. H. Compton and A. W. Simon, *ib.*, (2), **26**. 289, 1925; J. C. Boyce, *ib.*, (2), **23**. 575, 1924; K. T. Compton and C. H. Thomas, *ib.*, (2), **28**. 601, 1926; R. B. Jones, *ib.*, (2), **34**. 227, 1929; J. A. Becker, *ib.*, (2), **24**. 478, 1924; S. K. Allison and W. Duane, *ib.*, (2), **26**. 300, 1925; C. B. Bozzani and C. T. Chu, *Journ. Franklin Inst.*, **197**. 183, 1924; G. Kirsch and H. Pettersson, *Sitzber. Akad. Wien*, **134**, 491, 1925; W. G. Guy, *Abstract Theses Univ. Chicago*, **4**. 87, 1926; R. T. Dufford, *Journ. Amer. Opt. Soc.*, **18**. 17, 1929; G. L. Clark and W. Duane, *Proc. Nat. Acad.*, **10**. 92, 1924; V. Posejpal, *Compt. Rend.*, **182**. 767, 1926; M. de Broglie, *ib.*, **174**. 939, 1922; H. R. Robinson and A. M. Cassie, *Proc. Roy. Soc.*, **113**. A, 282, 1926; H. R. Robinson, *ib.*, **104**. A, 455, 1923; O. W. Richardson and F. C. Chalklin, *ib.*, **110**. A, 247, 1926; O. W. Richardson and F. S. Robertson, *ib.*, **115**. A, 280, 1927; **124**. A, 188, 1929; O. W. Richardson and S. R. Rao, *ib.*, **128**. A, 16, 1930; G. P. Thompson, *ib.*, **125**. A, 352, 1929; U. Nakaya, *ib.*, **124**. A, 616, 1929; G. B. Bandopadhyaya, *ib.*, **120**. A, 46, 1928; R. Hamer, *Journ. Amer. Opt. Soc.*, **9**. 251, 1924; L. P. Davis, *ib.*, **124**. A, 268, 1929; J. K. Roberts, *Proc. Roy. Soc.*, **129**. A, 146, 1930; G. I. Pokrovsky, *Zeit. Physik*, **63**. 561, 1930; R. Suhrmann and F. Breyer, *Phys. Zeit.*, **31**. 823, 1930; E. O. Lawrence and L. B. Linford, *Phys. Rev.*, (2), 35, 1492, 1930; (2), **36**. 482, 1930; A. Claassen, *Phil. Mag.*, (7), **9**. 57, 1930; T. Pavolini, *Ind. Chimica*, **5**. 1107, 1930; C. C. van Voorhis and K. T. Compston, *Phys. Rev.*, (2), **36**. 1435, 1930; N. Koboseff and N. I. Nebrassoff, *Zeit. Elektrochem.*, **36**. 529, 1930.

[12] J. Tsukamoto, *Nagoka's Anniv. Vol.*, 409, 1925; O. Feussner, *Zeit. Physik*, **25**. 215, 1924; O. Ruff, *Zeit. angew. Chem.*, **25**. 1889, 1912; M. von Pirani and G. Wangenheim, *Zeit. tech. Phys.*, **6**. 358, 1925; A. Denissov, *ib.*, **10**. 168, 1929; R. Becker and F. Born, *ib.*, **6**. 356, 1925; W. G. Guy, *Abstract Theses Univ. Chicago*, **4**. 87, 1926; P. Kapitza, *Proc. Roy. Soc.*, **105**. A, 691, 1924; **106**. A, 602, 1924; **115**. A, 658, 1927; **119**. A, 358, 1928; **123**. A, 292, 342, 1929; M. von Pirani, *Verh. deut. phys. Ges.*, **12**. 301, 1910; *Phys. Zeit.*, **13**. 753, 1912; B. Beckman, *ib.*, **18**. 507, 1917; P. E. Shaw and C. S. Jex, *Proc. Roy. Soc.*, **118**. A, 97, 1928; C. G. Fink, *Trans. Amer. Electrochem. Soc.*, **17**. 229, 1910; *Met. Chem. Engg.*, **8**. 341, 1910; *Chem. News*, **104**. 34, 1911; H. Pécheux, *Compt. Rend.*, **167**. 487, 1918; W. D. Coolidge, *Trans. Amer. Inst. Elect. Eng.*, **29**. 961, 1910; J. H. Dellinger, *Journ. Franklin Inst.*, **170**. 173, 1910; S. Weber, *Ann. Physik*, (4), **54**. 165, 1917; L. Holborn, *ib.*, (4), **59**. 145, 1919; *Zeit. Elektrochem.*, **25**. 334, 1919; *Zeit. Physik*, **8**. 58, 1922; O. M. Corbino, *Phys. Zeit.*, **11**. 413, 1910; **13**. 375, 1912; *Atti Accad. Lincei*, (5), **21**. i, 188, 1912; A. A. Somerville, *Phys. Rev.*, (1), **30**. 368, 532, 1910; (1), **31**. 261, 1911; I. Langmuir, *ib.*, (2), **7**. 302, 1916; H. A. Jones, *ib.*, (2), **28**. 202, 1926; A. G. Worthing, *Elect. World*, **59**. 861, 1912; *Phys. Rev.*, (1), **34**. 152, 1912; (2), **5**. 445, 1915; (2), **12**. 144, 1918; (2), **28**. 190, 1926; W. E. Forsythe and A. G. Worthing, *Astrophys. Journ.*, **61**. 146, 1925; *Phys. Rev.*, (2), **18**. 144, 1921; A. T. Waterman, *ib.*, (2), **22**. 259, 1923; *Phil. Mag.*, (7), **6**. 965, 1928; W. W. Coblentz, *Bull. Bur. Standards*, **6**. 109, 1909; A. Müller, *Zeit. angew. Chem.*, **27**. 545, 1914; E. F. Northrup, *Met. Chem. Engg.*, **11**. 45, 1913; *Elect. World*, **61**. 110, 1913; J. W. Avery and C. J. Smithells, *Proc. Phys. Soc.*, **39**. 85, 1926; T. J. Dillon, *ib.*, **41**. 546, 1929; H. E. Smith, *ib.*, **38**. 1, 1925; K. K. Smith, *Phil. Mag.*, (6), **29**. 802, 1915; W. Geiss, *Ann. Physik*, (4), **79**. 85, 1926; W. Geiss and J. A. M. van Liempt, *Zeit. anorg. Chem.*, **143**. 259, 1925; *Zeit. Physik*, **41**. 867, 1927; *Zeit. Metallkunde*, **17**. 194, 1925; A. Schulze, *ib.*, **15**. 159, 1923; **16**. 50, 1924; F. Koref, *ib.*, **17**. 213, 1925; H. A. Jones and I. Langmuir, *Gen. Elect. Rev.*, **30**. 310, 344, 1927; P. W. Bridgman, *Proc. Nat. Acad.*, **10**. 411, 1924; *Proc. Amer. Acad.*, **52**. 573, 1917; **58**. 166, 1923; W. M. Latimer, *Journ. Amer. Chem. Soc.*, **44**. 2136, 1922; C. Zwikker, *Versl. Akad. Amsterdam*, **34**. 468, 1925; *Proc. Acad. Amsterdam*, **28**. 498, 1925; *Arch. Néerl.*, (3), **9**. 207, 1925; S. Morugina, *Zeit. tech. Phys.*, **7**. 486, 1926; G. Borelius, *Nature*, **109**. 613, 1922; *Ann. Physik*, (4), **68**. 67, 1922; E. D. Williamson, *Journ. Franklin Inst.*, **193**. 491, 1922; S. Smith, *Astrophys. Journ.*, **61**. 186, 1925; *Proc. Nat. Accad.*, **10**. 4, 1924; K. Höjendahl, *Phil. Mag.*, (6), **48**. 349, 1924; E. Güneisen and E. Goens, *Zeit. Physik*, **44**. 615, 1927; H. Rolnick, *Phys. Rev.*, (2), **36**. 506, 1930; U. Fischer, *Zeit. phys. Chem.*, **8**. B, 207, 1930; I. Langmuir, S. MacLane and K. B. Blodgett, *Phys. Rev.*, (2), **35**. 478, 1930; J. C. McLennan, L. E. Howlett and J. O. Wilhelm, *Trans. Roy. Soc. Canada*, (3), **23**. 287, 1930; H. K. Onnes and W. Tuyn, *Comm. Phys. Lab. Leiden*, Suppl. 58, 1926; A. Günther-Schulze, *Ann. Physik*, (4), **65**. 223, 1921; G. Tammann and M. Staumanis, *Zeit. anorg. Chem.*, **169**. 365, 1928; I. Langmuir and K. H. Kingdon, *Phys. Rev.*, (2), **34**. 129, 1929; W. B. Reynolds, *ib.*, (2), **35**. 158, 1930; M. Forro and E. Patai, *Zeit. Physik*, **63**. 444, 1930; R. Saxon, *Chem. News*, **132**. 170, 1926; W. Rohn, *Zeit. Metallkunde*, **16**. 297, 1924; E. Blumenthal, *Ann. Physik*, (5), **7**, 470, 1930.

[13] A. Thiel and W. Hammerschmidt, *Zeit. anorg. Chem.*, **132**. 15, 1923; R. D. Kleeman and W. Frederickson, *Phys. Rev.*, (2), **19**. 409, 1923; I. Langmuir and K. H. Kingdon, *ib.*, (2), **34**. 129, 1929; A. S. Russell and S. W. Rowell, *Journ. Chem. Soc.*, 1881, 1926; W. E. Koerner, *Met. Chem. Engg.*, **15**. 522, 1916; **16**. 40, 1917; *Trans. Amer. Electrochem. Soc.*, **30**. 222, 1916; **31**. 221, 1917; S. J. French and L. Kahlenberg, *ib.*, **54**. 163, 1928; A. Fischer, E. K. Rideal and A. Roderburg, *Zeit. anorg. Chem.*, **81**. 170, 1916; A. Roderburg, *Das elektrochemische Verhalten des Wolframs*, Aachen, 1912; O. W. Richardson and F. S. Robertson, *Phil. Mag.*, (6), **43**. 162, 1922; M. le Blanc and H. G. Byers, *Zeit. phys. Chem.*, **69**. 19, 1909; A. Coehn and O. Schafmeister, *ib.*, **125**. 401, 1927; E. Newbery, *Journ. Chem. Soc.*, **109**. 1066, 1916; W. de Groot, *Physica*, **5**. 121, 234, 1925; W. Muthmann, *Zeit. Elektrochem.*, **10**. 521, 1904; W. Muthmann and

F. Fraunberger, *Sitzber. Bayr. Akad.*, 201, 1904; O. Sackur, *Chem. Ztg.*, **28**. 954, 1904; E. S. Davenport, *Trans. Amer. Inst. Min. Eng. Metals Div.*, 413, 434, 1927; M. Katalinic, *Zeit. Physik*, **14**. 14, 1923; R. Saxon, *Chem. News*, **132**. 170, 1926; W. Wehrli, *Zeit. Physik*, **44**. 301, 1927; L. W. Walter, *Journ. Inst. Elect. Eng.*, (2), **43**. 547, 1908; (2), **44**. 373, 1909; *Electrician*, **63**. 991, 1909; S. Dushman, *Gen. Elect. Rev.*, **18**. 156, 1915; G. S. Meikle, *ib.*, **19**. 297, 1916; R. E. Russell, *ib.*, **20**. 209, 1917; E. Blechschmidt, *Ann. Physik*, (4), **81**. 999, 1926; A. L. Clark, *Trans. Roy. Soc. Canada*, (3), **18**. 275, 1924; J. Taylor, *Proc. Roy. Soc.*, **114**. A, 73, 1927; H. H. Willard and F. Fenwick, *Journ. Amer. Chem. Soc.*, **44**. 2504, 1922; W. B. Nottingham, *Phys. Rev.*, (2), **27**. 806, 1926; (2), **28**. 764, 1926; (2), **31**. 711, 1928; S. H. Anderson and G. G. Kretchmar, *ib.*, (2), **26**. 33, 1925; E. K. G. Stueckelberg, *ib.*, (2), **31**. 771, 1928; C. del Rosario, *Journ. Franklin Inst.*, **205**. 103, 1928; H. Nagaoka and T. Futagami, *Proc. Acad. Tokyo*, **3**. 643, 647, 1927; **4**. 201, 1928; A. Günther-Schulze, *Ann. Physik*, (4), **65**. 223, 1921; L. B. Flexner and E. S. G. Barron, *Journ. Amer. Chem. Soc.*, **52**. 2773, 1930; P. Bächtiger, *Helvetica Phys. Acta*, **3**. 335, 1930; O. Bauer, *Internat. Zeit. Metallog.*, **10**. 129, 1919; J. S. Forrest, *Phil. Mag.*, (7), **10**. 1003, 1930.

[14] H. Moissan, *Compt. Rend.*, **123**. 13, 1896; *Ann. Chem. Phys.*, (7), **8**. 570, 1896; K. Honda, *Ann. Physik*, (4), **32**. 1027, 1910; M. Owen, *ib.*, (4), **37**. 657, 1912; S. Meyer, *Wied. Ann.*, **68**. 324, 1899; *Monatsh.*, **20**. 369, 1899; L. Weiss, *Zeit. anorg. Chem.*, **65**. 279, 1910; D. M. Bose and H. G. Bher, *Zeit. Physik*, **48**. 716, 1928; P. Kapitza, *Proc. Roy. Soc.*, **123**. A, 292, 342, 1929.

§ 6. The Chemical Properties of Tungsten

Owing to the effects of passivity, and the effects of ignored impurities, descriptions of the chemical behaviour of tungsten are not always consistent. F. Fisher and F. Schrötter[1] observed that no combination occurs when tungsten is disintegrated electrically beneath liquid **argon.** According to A. Sieverts and E. Bergner, **hydrogen** is very little absorbed by tungsten below 1200°. E. Martin studied the occlusion of hydrogen by the metal. I. Langmuir showed that if a tungsten wire is heated at 1300° K. to 1500° K. in hydrogen under a press. of 0·001–0·020 mm., the hydrogen slowly disappears. There is a distinct fatigue effect, but the substitution of a new section of wire does not restore the action. The hydrogen is not absorbed by the wire, but is deposited on the glass, especially if the latter is cooled by liquid air. On allowing the wire to cool and then removing the liquid air, hydrogen is liberated, and does not re-condense if the liquid air is replaced. If the hydrogen is now pumped out and oxygen admitted, the oxygen will disappear and be replaced by a small quantity of hydrogen. It is suggested that the hydrogen dissolves in the wire in the atomic condition, and that some of the atoms, leaving the wire, diffuse into the tube cooled by liquid air, or become adsorbed by the glass, and remain in the atomic conditions, thus retaining their chemical activity. M. A. Schirmann utilized the property of tungsten for absorbing the last traces of gas in order to convert a high vacuum into an extreme vacuum. T. Weichselfelder and B. Thiede obtained a **tungsten hydride,** presumably WH_3, analogous with CrH_3, by shaking dry hydrogen with an ethereal soln. of phenyl magnesium bromide in which the dry chloride of the metal is suspended. G. Hägg studied the mol. vol.

The finely-divided metal was found by J. Férée to be pyrophoric in **air**; and E. Zettnow, and L. von Uslar found that when the finely-divided metal is heated, it becomes dark blue, and then suddenly glows to form tungsten trioxide. A. Burger found the metal produced by the calcium reduction oxidizes in air when heated to 300° or 400°. A. Riche found that the crystalline powder is not changed by a month's exposure to dry or moist **oxygen** at ordinary temp., but at a red-heat, it burns to the trioxide; a similar result is obtained at a rather higher temp. in air. E. R. Schneider added that the volume is at the same time markedly increased. A. Stavenhagen, L. Weiss, and H. Moissan observed that the metal prepared in the electric arc-furnace is stable in air after it has acquired a blue oxide film. N. B. Pilling and R. E. Bedworth discussed the rate of oxidation; and L. O. Bannister, the coloured oxide films. N. B. Pilling and R. E. Bedworth found that the weight w of oxygen taken up by a metal in the time t is in accord with the parabolic oxidation law $w^2=kt$, where k is a constant. They gave 3·30 for the critical density ratio—*vide* iron. With most metals, J. S. Dunn found that k

increases regularly with temp. in accord with $k=ae^{b/RT}$, where a and b are constants, and e, R, and T have their usual meaning. J. S. Dunn found an irregularity in the curve showing the values of log k at different temp., as indicated in Fig. 19. This is explained by the assumption that tungstic oxide is not a chemical individual, but consists of a mixture of α-WO_3 and β-WO_3, and the equilibrium between the two is shifted with rise of temp. The β-form, produced in excess at the higher temp., is less permeable to oxygen than is the α-form, and a kink occurs in the curve in the range of temp. on which the change from an excess of the β-form to an excess of the α-form occurs. E. Zettnow observed that the metal prepared at a white-heat oxidizes at a red-heat only with difficulty, while that prepared at a red-heat, readily oxidizes under these conditions, and the finely-divided metal obtained by reducing the oxide with sodium is partially oxidized during the washing and drying. M. A. Schirmann studied the production of vacua by absorbing oxygen on the surface of a tungsten filament heated in oxygen at a low press. C. G. Fink found that drawn wires of ductile tungsten retain their lustre indefinitely long in air; and L. Weiss added that compact tungsten is very little affected by air. When heated, a superficial film of oxide is formed which is not much affected by one or two hours' heating to redness.

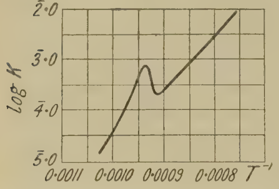


FIG. 19.—The Rate of Oxidation of Tungsten at different Temperatures.

The metal with a conchoidal fracture is more resistant towards chemical agents—particularly oxidation—than is that with a granular fracture. According to I. Langmuir, when a tungsten wire is heated in oxygen at a low press. it oxidizes to WO_3 at about 800° K., but on raising the temp. to 1200° K. the oxide volatilizes, and leaves the metal clean and bright. At temp. above 1200° K. oxygen at press. below 0·02 mm. acts on a tungsten wire at a rate which is proportional to the press. of the oxygen and the surface of metal exposed, and increases rapidly with the temp. No fatigue effect can be observed. The velocity is not affected by varying the temp. of the bulb.

L. von Uslar said that the metal obtained by the thermal decomposition of tungsten oxychlorides by hydrogen is not affected by many weeks contact, with cold or hot **water.** J. J. and F. de Elhuyar, and A. Riche also observed that water has no action on tungsten; but at a red-heat, water vapour oxidizes tungsten forming a mixture of the trioxide and the blue oxide. C. J. Smithells and co-workers found that with an incandescent tungsten filament in water vapour, the metal is oxidized at the hotter parts of the filament, and the oxide is reduced to metal in the cooler parts: $W+2H_2O \rightleftharpoons WO_2+2H_2$. The atomic hydrogen also formed, as shown by I. Langmuir, can reduce tungstic oxide at ordinary temp. L. Wöhler and W. Prager studied the influence of steam on tungsten; the reaction $W+2H_2O \rightleftharpoons WO_2+2H_2$ is a balanced one, in which the equilibrium constant $K=p_{H_2O}/p_{H_2}$ is 0·65 at 828°; 0·82 at 868°; 0·99 at 941°; and 1·29 at 1036°. The reaction was studied by W. Reinders and A. W. Vervloet, etc.—*vide supra*, the reduction of tungsten trioxide to metal. H. Alterthum and R. Becker studied the formation of fogs—aerosols of tungsten oxides, formed in tungsten filament lamps by the action of oxygen or water-vapour. W. Guertler and T. Liepus observed no action by sea-water, sea-water and air, or rain-water and air in 8 days; nor any reaction by a soln. of **hydrogen dioxide** in soda-lye in 48 hrs. L. J. Thénard said that the reaction is at first feeble, but later is more vigorous, part of the oxygen escapes free and part oxidizes the metal. A. Lottermoser studied the catalytic decomposition of hydrogen dioxide by tungsten. C. G. Fink observed that tungsten is rapidly attacked when heated with **sodium dioxide**; and H. Moissan, that it is also attacked by **lead dioxide.**

According to H. Moissan, **fluorine** attacks tungsten, at ordinary temp., with incandescence forming a volatile fluoride. A. Riche, H. Davy, and L. Weiss observed that, at 250°–300°, dry **chlorine,** free from air, forms the hexachloride, but if air or moisture be present, two oxychlorides are formed. I. Langmuir found that when chlorine, under a low press., is contained in a bulb with a heated tungsten filament, the metal is attacked with the formation of the hexachloride. The velocity of the reaction reaches a maximum at about 1500° K., and becomes very small at higher temp. W. Guertler and T. Liepus, and L. von Uslar found that tungsten is not attacked by chlorine-water in 8 hrs. A. Riche, and H. E. Roscoe observed that tungsten at a bright red-heat is attacked by **bromine** forming, according to J. B. von Borck, the pentabromide; if air moisture be present, A. Riche observed that an oxybromide is formed; and tungsten at a red-heat unites with **iodine,** forming, according to A. E. Roscoe, the diiodide. L. Weiss observed that bromine and iodine superficially attack the metal at a red-heat. V. I. Spitzin and L. Kaschtanoff said that tungsten at 500° to 600° is not attacked by **hydrogen chloride.** According to W. E. Ruder, neither hot nor cold **hydrofluoric acid** attacks tungsten; nor is the surface of the polished metal dulled when evaporated with the acid. H. Moissan also observed that hydrofluoric acid has but a slight action on tungsten; and similarly also with hydrochloric acid. J. J. and F. de Elhuyar said that this acid has no action; and A. Riche, that there is a slow action and the liquid becomes blue. C. G. Fink added that ductile tungsten is but slowly attacked; and L. Weiss that the compact metal is not attacked by the dil. or conc. acid. W. Guertler and T. Liepus observed no action by 10 or 50 per cent. hydrochloric acid in 8 hrs. W. Rohn said that while 10 per cent. acid had no action in 24 hrs., the hot acid dissolved 0·01 per cent. in an hour. According to W. E. Ruder, wrought tungsten is insoluble in hydrochloric acid of any conc. at room temp. and only very slightly so at 110°. After 45 hrs., hot conc. acid of sp. gr. 1·15 showed no effect upon the tungsten. After 175 hrs., however, a black coating of oxide formed and the metal lost 0·5 per cent. in weight. In dil. acid, at 110°, it lost 0·05 per cent. after 22 hrs., but showed no further loss after 50 hrs. After 175 hrs. the metal was coated with tungstic oxide and there was a gain in weight of 1 per cent. due to oxidation. This oxide formed an adherent coat and protected the metal against further loss.

A. Riche, and J. B. von Borck found that molten or boiling **sulphur** acts slowly on the metal. According to E. F. Smith and H. Fleck, tungsten is not acted on by **sulphur monochloride,** but if chlorine be present, tungsten hexachloride is formed. N. Domanicky classed tungsten with the metals either not acted on by sulphur monochloride, or else acted on with extreme slowness. E. F. Smith and V. Oberholtzer found that the vapour of sulphur monochloride forms a sulphochloride. A. Rich observed that the vapour of **carbon disulphide** transforms heated tungsten into the disulphide; L. Weiss, that **hydrogen sulphide** darkens the surface of tungsten at a red-heat, but it produces no marked change. J. Férée found that the pyrophoric metal becomes red-hot forming the sulphide when it is exposed to a current of hydrogen sulphide. W. Guertler and T. Liepus observed no reaction by a 10 or 50 per cent. soln. of **sodium sulphide** in 48 hrs., or by a 4 per cent. soln. of sodium sulphide containing 8 per cent. alkali in 8 hrs. C. H. Ehrenfeld observed that **sulphur dioxide** forms a little blue, green, or brown oxide; and J. Férée, that pyrophoric tungsten becomes red-hot in hydrogen sulphide or in sulphur dioxide, forming tungsten sulphide. E. D. Desi said that **sulphurous acid** acts on tungsten to form the 5 : 14-oxide (*q.v.*). J. J. and F. de Elhuyar said that **sulphuric acid** has no action on tungsten; H. Moissan, that there is a slight action forming, according to A. Riche, a blue liquid; C. G. Fink, that the action of sulphuric acid on the ductile metal is very slow; L. Weiss, that while dil. sulphuric acid is without action, the conc. acid forms a blue liquid; and E. D. Desi, that the conc. acid at a high temp. forms sulphur dioxide and some intermediate tungsten oxides (*q.v.*). R. H. Adie said that sulphur dioxide appears at 175°, but no hydrogen sulphide. W. E. Ruder observed that sulphuric acid, at room temp., has no effect upon wrought tungsten nor has the dil. acid at 110°. Conc. acid attacks it very slowly at 110°, the loss in weight being 0·1 per cent. after 18 hrs., 0·16 per cent. after

40 hrs., and 0·63 per cent. after 175 hrs. At a higher temp. the action is hastened, for at 200°, 0·62 per cent. was lost in 4 hrs. In another experiment 1·18 per cent. dissolved in 8 hrs. W. Guertler and T. Liepus observed no reaction in 8 hrs. with a 10 per cent. sulphuric acid, or 20 per cent. sulphuric acid sat. with sodium sulphate. W. Rohn found that 10 per cent. sulphuric acid had no action in 24 hrs. in the cold; 0·01 per cent. dissolved in the hot acid in an hour. C. G. Fink observed that fused **potassium hydrosulphate** readily attacks the metal.

H. Moissan found that **nitrogen** at a red-heat does not attack tungsten; and A. Sieverts and E. Bergner, that there is no reaction at 1500°. E. Martin studied the absorption of nitrogen by the metal. C. J. Smithells and H. P. Rooksby found that the dinitride is formed by an incandescent tungsten filament in nitrogen. I. Langmuir showed that when a tungsten lamp containing nitrogen at low press. is run for some time, the nitrogen gradually disappears—*vide* tungsten nitride, **8**. 49, 12. N. R. Campbell made some observations on this subject; and M. A. Schirmann discussed the production of vacua by this means. C. Kenty and L. A. Turner studied the effect of surface layers of active nitrogen on tungsten filaments; and observed that a clean tungsten surface, at a dull red-heat, in an atm. of activated nitrogen, becomes covered with a layer of nitrogen one-atom deep. I. Zschukoff observed no reaction with tungsten and nitrogen below 1250°. E. J. B. Willey measured the rate of decay of active nitrogen in the presence of a tungsten filament. C. Matignon and E. Desplantes observed that when the finely-divided metal is shaken up in a flask with 10 c.c. of aq. **ammonia** at ordinary temp., the metal is oxidized. W. Guertler and T. Liepus observed no action with 10, 50, or 70 per cent. soln. of ammonia in 48 hrs.; but S. L. Malowan found that the metal is attacked. C. H. Kunsman and co-workers, and F. Hahn used tungsten as a catalyst in the synthesis of ammonia (*q.v.*); C. H. Kunsman, and R. E. Burk studied the action of tungsten on ammonia. F. W. Bergstrom observed little if any reaction with **potassamide.** C. H. Ehrenfeld found that when heated with **nitrous oxide,** tungsten trioxide is formed. Similarly with **nitric oxide,** and, added F. Emich, the action of nitric oxide is very similar to that of oxygen provided the temp. of the former gas is kept below red-heat, the temp. of decomposition. C. H. Ehrenfeld found that **nitrogen peroxide** when heated with tungsten oxidizes it to tungsten trioxide. J. J. and F. de Elhuyar, L. von Uslar, E. Zettnow, A. Riche, and H. Moissan observed that tungsten is easily oxidized by warm **nitric acid** to yellow tungsten trioxide. C. G. Fink observed that the ductile metal is but slowly attacked; and L. Weiss, that the compact metal is superficially oxidized by hot nitric acid, or aqua regia. A. Stavenhagen, and L. von Uslar said that the metal is not attacked if heated many days with fuming nitric acid, or with aqua regia. According to W. E. Ruder, conc. nitric acid at 110° shows no action after 48 hrs. other than a slight dulling of the bright, metallic surface. The dil. acid, however, produces the yellow oxide on the surface. There is a slight gain in weight after 15 hrs. and then no further change even after 175 hrs.' immersion. J. J. and F. de Elhuyar, A. Riche, and H. Moissan found that it is readily oxidized to tungsten trioxide by aqua regia. W. E. Ruder found that aqua regia at room temp. oxidizes the surface of tungsten to the trioxide. After 215 hrs. the loss in weight was 0·31 per cent. At 110°, the chlorine was all driven off in about 4 hrs. and the tungsten disc had lost 0·1 per cent. and it was covered by a tough, greenish-yellow deposit. If this coating of oxide was allowed to remain, continued boiling in fresh aqua regia had no further effect upon the metal. W. Guertler and T. Liepus observed no action in 24 hrs. with 50 per cent. nitric acid, or with hot or cold, 10 per cent. acid; nor did aqua regia have any action. W. Rohn added that 10 per cent. nitric acid had no perceptible action in 8 hrs. in the cold, the hot acid dissolved 0·06 per cent. in one hour. W. E. Ruder, and H. Moissan found that a mixture of nitric and hydrofluoric acids rapidly dissolves tungsten with the evolution of nitric oxide, and the production of tungsten trioxide. L. Weiss added that the tungsten dissolves as hexafluoride or oxytetrafluoride. H. Moissan, and C. G. Fink observed that fused **sodium nitrate** readily attacks the metal. H. Moissan found that **phosphorus** does not combine with tungsten at a red-heat, but they react at a high temp. W. Rohn found that a 10 per cent. soln. of **phosphoric acid** dissolves 0·03 per cent. of tungsten in the cold in 24 hrs., and if hot, 0·001 per cent. in one hour. M. Wunder and B. Janneret also noted the dissolution of tungsten by phosphoric acid of sp. gr. 1·75, at 230°.

H. Moissan observed that when tungsten is heated with **boron** in the electric furnace, a boride is formed which rarely scratches the ruby; and similarly with **silicon.** When the metal is heated with **carbon,** it readily undergoes cementation. A. Riche, and C. W. Siemens and A. K. Huntington noted that the metal dissolves carbon; and H. Moissan, that 18·8 per cent. of carbon can be dissolved by tungsten. G. Tammann and K. Schönert, C. Zwikker, and M. R. Andrews and S. Dushman studied the diffusion of carbon in tungsten; and W. Geiss and J. A. M. van Liempt found that carbon diffused into a pressed bar at 1500°; but not into a single crystal at 1900°. M. R. Andrews, O. Ruff, G. Agte and H. Alterthum, and A. Westgren and G. Phragmen studied the action of carbon on tungsten. M. A. Schirmann studied the production of vacua by absorption of carbon monoxide at a low press. in bulbs containing a heated tungsten filament. S. Hilpert and M. Ornstein found that when the finely-divided metal is heated in **methane**—mixed with hydrogen to suppress the dissociation: $CH_4 \rightleftharpoons C+2H_2$—the carbide WC is formed at 800°; and when heated in **carbon monoxide** at 1000°, the carbide W_3C_4 is formed. According to I. Langmuir, if a tungsten filament is heated at 2200° K. in carbon monoxide under a press. of 0·001–0·020 mm., the gas slowly disappears. The behaviour of the gas resembles that of nitrogen; each atom of tungsten combines with one mol. of carbon monoxide, probably with formation of a compound, WCO. The rate of attack is independent of the press., probably owing to the velocity of the reaction being so great that the rate of evaporation of the compound formed determines the rate of reaction. The temp. coeff. of the reaction velocity is strongly negative. The interaction of carbon dioxide and hydrogen on the surface of tungsten was studied by C. N. Hinshelwood and C. R. Prichard, and B. S. Srikantan. J. Férée observed that tungsten when pyrophoric becomes red-hot in carbon monoxide. W. Guertler and T. Liepus observed no action by **carbon dioxide** and air after an exposure of less than 8 hrs. At 1200°, tungsten forms a blue oxide when heated with carbon dioxide; and water saturated with carbon dioxide slowly attacks the metal. Molten sodium carbonate dissolves tungsten slowly, but a fused mixture of sodium carbonate and nitrate dissolves it rapidly. According to W. E. Ruder, tungsten is slowly dissolved by fused sodium or potassium carbonate, or by mixtures of the two. A loss of about 2·5 per cent. was noticed in 4 hrs.; and when potassium nitrate was present, the loss was 32 per cent. in 6 hrs. C. Beindl used tungsten as a catalyst in the synthesis of hydrocyanic acid from nitrogen, hydrogen, and carbon monoxide. M. R. Andrews and S. Dushman found that **naphthalene** is decomposed by incandescent tungsten above 1500°. W. Rohn observed that 10 per cent. **acetic acid** has no action on tungsten; and W. Guertler and T. Liepus observed no action by acetic acid in 48 hrs., or by **citric acid,** or **tartaric acid** in 24 hrs. The Regina Bogenlampenfabrik found that finely-divided tungsten rapidly absorbs 6 to 10 per cent. of **pyridine** or **quinoline.** The products were used in the preparing lamp filaments. P. C. Allen and C. N. Hinshelwood, and A. Korcynsky studied tungsten as a catalyst in reactions with organic compounds; and O. Schmidt, as a hydrogenation catalyst.

The compounds of tungsten with the **metals** are discussed below. According to A. Riche, S. L. Malowan, and S. M. Delepine and L. A. Hallopeau, water made feebly alkaline with potassium hydroxide dissolves a little tungsten, forming the alkali tungstate; a conc. soln. of **potassium hydroxide** rapidly dissolves tungsten without giving off any hydrogen. L. von Uslar said that the boiling lye does not attack the metal, and W. E. Ruder observed that a soln. of potassium hydroxide of any conc. does not attack wrought tungsten, but the fused alkali attacks the metal slowly. In this case there was 31 per cent. loss in weight after 15 hrs., and in about 40 hrs. the disc had all dissolved. A. Stavenhagen also observed that the metal is slowly dissolved by the fused alkali, forming, according to S. Hilpert and M. Ornstein, traces of potassium and hydrogen, $W+6KOH \rightarrow W(OH)_6+6K$; $W(OH)_6+2KOH \rightarrow K_2WO_4+4H_2O$; and $4K+4H_2O \rightarrow 4KOH+2H_2$. W. Guertler and T. Liepus observed no action by a 10 or 50 per cent. soln. of **sodium hydroxide** in 48 hrs. W. E. Ruder said that a soln. of **chromium trioxide** in sulphuric acid does not attack tungsten. For the action of **alkali carbonate,** *vide supra.* A. von Wartenberg and H. Möhl found that tungsten reduces **alumina** at 2000° in an atm. of nitrogen, forming tungsten dioxide : $4Al_{gas}+3WO_{2gas}=3W+2Al_2O_3+700$ cals., or, if the alumina is vaporized, $4Al_{gas}+3WO_{2gas}=3W+2Al_2O_{3gas}+570$ cals., because the heat of vaporization of alumina is —130 Cals. Hence, in the former case, if $K=[Al]^4[WO_2]^3$, then $\log K=-153000T^{-1}+12{\cdot}3 \log T+21$; and, in the latter case, if $K'=[Al]^4[WO_2]^3/[Al_2O_3]^2$, $\log K'=-12450T^{-1}+8{\cdot}75 \log T+15$. In the former case, at 2500° and 3000°, log K is respectively 3 and 13, and in the latter case, log K' is respectively 0 and 3·5 at these temp. In the case of **zirconia,** $Zr_{gas}+WO_{2gas}=W+ZrO_2+150$ cals., and if $K=[Zr][WO_2]$, then $\log K=-3300T^{-1}+3{\cdot}5 \log T+6$, and at 2500° and 3000°, log K is respectively 5 and 7. Similarly with **thoria** which is also reduced by tungsten. According to C. J. Smithells, at 2580° K., no reaction was perceptible between tungsten and thoria in 24 hrs. ; at 2600° K., some reaction occurred ; and at 2750° K., the thoria was completely reduced by the tungsten. Z. Jeffries and P. Tarsov found that a little thorium is produced by dissociation when a thoriated tungsten filament is heated to a high temp. Thoria is slightly soluble in tungsten at high temp. The behaviour of thoria on heated tungsten filaments was discussed by W. G. Burgers and J. A. M. van Liempt. W. Samter and K. Schröter found that tungsten is dissolved by a bath of fused **sodium nitrite and nitrate.** W. Guertler and T. Liepus observed no reaction by a soln. of **magnesium chloride** in 8 hrs. E. F. Smith found that tungsten precipitates copper incompletely from a soln. of a **copper salt ;** and it behaves like molybdenum towards soln. of **silver salts,** precipitating silver, but the action of tungsten on soln. of **gold salts** is somewhat slower than that of molybdenum. Tungsten slowly reduces a soln. of **mercuric chloride** to mercurous chloride ; W. Guertler and T. Liepus observed that a soln. of mercuric chloride (1 : 500) is decomposed by tungsten at 90°. The subject was also studied by J. S. de Benneville. E. F. Smith found that soln. of **cadmium salts** and of **bismuth salts** are not affected by tungsten ; and the metal has no action on neutral, alkaline, or acidic soln. of lead salts.

C. G. Gmelin [2] made some observations on the physiological action of tungsten salts.

Some reactions of analytical interest.—The reactions of tungsten were discussed by A. A. Noyes and W. C. Bray,[3] and F. L. Hess. The **mineral acids**—hydrochloric, sulphuric, and nitric acids—with a soln. of sodium tungstate produce in the cold a white, amorphous precipitate of hydrated tungsten trioxide ; and when the soln. is boiled, the precipitate becomes yellow owing to the formation of yellow tungstic acid, which is insoluble in dil. acids, but appreciably soluble in conc. acids. Free tungstic acid slowly dissolves in a boiling soln. of an alkali tungstate forming a metatungstate which does not give a precipitate with mineral acids. If the soln. of a metatungstate is boiled with an excess of acid, insoluble tungstic acid is slowly precipitated. With **phosphoric acid,** soln. of the alkali tungstates give a precipitate of a complex alkali phosphatotungstate which is soluble in an excess of phosphoric acid. The presence of phosphoric acid hinders the precipitation of tungstic acid by the mineral acids. Many **organic acids**—*e.g.* citric and tartaric acids—give no precipitate with alkali tungstates owing to the formation of stable, soluble complex salts, and they hinder the precipitation of tungstic acid by mineral acids, they also interfere with the action of several other reagents—*e.g.* reducing agents. No precipitate is formed when acidified soln. are treated with **hydrogen sulphide ;** and **ammonium sulphide** gives no precipitate, but, according to W. T. Taggart and E. F. Smith, if a salt—*e.g.* manganese salt—is present which gives a precipitate with ammonium sulphide, tungsten sulphide may be precipitated. If the soln. containing an excess of ammonium sulphide be treated with an acid, light brown tungsten trisulphide is precipitated; it is soluble in a soln. of ammonium sulphide. Soln. of the tungstates give white precipitates with soln. of **barium or calcium chloride, lead acetate,** and **silver or mercurous nitrate.** E. Zettnow added that one part of tungstic acid in 20,000 parts of water gives a white coloration with lead acetate; and with 1 in 40,000, an opalescence. A brown precipitate is produced by tincture of galls, or **tannin** when the soln. is acidified (M. Barber). The effect of **reducing agents** is to form a blue coloration—*e.g.* if a soln. of an alkali tungstate is treated with zinc and hydrochloric acid, the tungstic acid first precipitated forms blue tungsten hemipentoxide; stannous chloride first produces a yellow coloration, but when hydrochloric acid is added and the soln. warmed, a blue precipitate is formed. E. Zettnow added that one part of tungstic acid in 1000 parts of water treated with sulphuric acid and stannous chloride gives a brownish-yellow colour; with 1 in 10,000, the colour is white; and with 1 in 20,000 a pale opalescence is produced. Sodium hypophosphite, and sulphurous acid in a warm acidified soln. produce a blue coloration; **dihydroxymaleic acid** forms a brown colour which immediately turns blue (H. J. H. Fenton); mercurous nitrate and potassium iodide give a blue coloration (E. Kafka, and E. Pozzi-Escot); but with ferrous sulphate, the ochre-yellow precipitate is not coloured blue by acids. The reduction test was discussed by G. Torossian, and M. L. Hartmann. J. H. Muller observed that salicylic acid gives a yellow coloration with alkali tungstates and molybdates but no precipitate; and J. H. de Boer, that **alizarin sulphonic acid** gives a violet coloration. According to E. F. Smith, quinine sulphate, and chloride, and cinchonidine, and benzidine hydrochloride, acetate, and chloride precipitate tungstic acid quantitatively from soln. of its salt. Aniline hydrochloride does not give a precipitate with sodium and ammonium tungstates, and metatungstates, but does so with the paratungstates but not after boiling. The three sodium and ammonium tungstates are incompletely precipitated by *o*-toluidine and pyridine hydrochlorides. A little tungstic acid gives a deep reddish-brown coloration with **potassium ferrocyanide,** and after some time a reddish-brown jelly. E. Zettnow said that one part of tungsten trioxide in 1000 parts of water acidified with a little sulphuric acid gives a dark orange-yellow colour; with 1 in 10,000, a greenish-yellow colour; and with 1 in 20,000, a pale yellow colour.

Some uses of tungsten.—Some unique properties of tungsten have important industrial applications.[4] It has a high density exceeding that of lead. Its m.p. is higher than that of any known metal; its tensile strength exceeds that of iron and nickel; it is paramagnetic and elastic so that it has been tried in electrical meters, and non-magnetizable watch-springs. It can be drawn into thinner wires than any other metal, and this fact, coupled with its chemical stability, offers possibilities in making suspensions for galvanometer needles,[5] and cross-hairs for telescopes; and for thin wires in surgical operations in place of gold or silver wires. The greatest use of tungsten is in the preparation of iron or steel alloys, *e.g.* in the preparation of high-speed tool steels (*q.v.*). Tungsten forms alloys with many of the metals, and some of them have valuable properties although in many cases the cost of the alloy is out of proportion with its usefulness. The *stellite* alloy described by E. Haynes[6] is an alloy of cobalt, chromium, and tungsten (75 : 20 : 5) with or without additions of other metals. It is a competitor for some high-speed cutting steels. J. T. Bottomley proposed an alloy called *platinoid,* composed of nickel, zinc, copper, and tungsten for conductivity wires. E. Weintraub patented an alloy with 40 to 80 per cent. of platinum for use in electrical contacts, jewellery, etc. *Partinium* is an alloy of aluminium and tungsten employed in automobile construction; *sideraphite,* an alloy of iron with nickel, copper, aluminium and tungsten; *minargent,* an alloy of copper, nickel, and tungsten; and *backford,* an alloy of copper, tin and tungsten. F. A. Fahrenwald discussed the use of alloys of tungsten and molybdenum as substitutes for platinum for contact points in sparking coils, voltage regulators, and other electrical instruments. Gold-coated tungsten dental pins are also used in place of platinum. E. Groschuff and F. Mylius found that malleable tungsten under the trade-name *iridam*, proposed as a substitute for platinum, is too brittle for thin-walled crucibles, and it is attacked by hydrochloric acid. According to E. Haynes, an alloy of tungsten, chromium, and cobalt (20 : 15 : 65) is hard, and can be used for cutting tools and surgical instruments, being unaffected by organic acids and ordinary antiseptics. A similar alloy with nickel is called *amaloy*. P. Monnartz discussed the use of tungsten in raising the acid resisting properties of iron-chromium alloys. The alloys of tungsten were discussed by H. Mennicke, H. Leiser, A. Hoenig, J. W. Richards, J. S. de Benneville, J. J. Runner and M. L. Hartmann, etc.—*vide infra*. The use of tungsten as a filament in incandescent lamps has been previously discussed. J. Trowbridge and S. Sheldon [7] recommended tungsten as an alloy metal for mirrors in physical apparatus. The use of tungsten as a valve electrode and as a rectifier has been previously indicated. W. Fehse [8] recommended it for resistance wires for the Tungsten arc-lamp as a source of ultra-violet light; [9] and tungsten anode in the mercury lamp [10] have been tried. Tungsten wire has also been used as a resistor in wire-wound electrical furnaces—*e.g.* by F. Fischer and E. Tiede,[11] A. H. Compton, and F. A. Fahrenwald. The " metal," widia, is obtained by pressing and sintering tungsten carbide alloyed with cobalt.[12] R. Eisenmann [13] used tungstic acid as a substitute for chromic acid in the chromic acid cell; J. Harden,[14] and J. H. Robertson and D. Jankower used tungsten for making crucibles. Wrought tungsten targets for X-ray tubes are in general use. The high sp. gr. of the metal is here an advantage.[15] The targets are sometimes made with a surface of tungsten on a backing of some other metal, as silver or copper which conducts away the heat more rapidly. Colloidal tungsten was recommended by R. Kruger [16] as a substitute for bismuth in X-ray photographs of the gastro-intestinal canal. Calcium or cadmium tungstate [17] is used with the addition of, say, sodium vanadate to prevent the glare on fluorescent screens on X-ray work.

Tungsten has been tried by F. Haber,[18] as a catalyst in the manufacture of hydrogen cyanide ; and C. Beindl used it with good results as a catalytic agent in the synthesis of ammonia ; in the interaction of hydrogen and carbon dioxide ; [19] in the splitting of alcohol into ethylene and water ; [20] and in organic combustion analyses.[21] There are some miscellaneous applications of tungsten compounds in the chemical laboratory [22]—*e.g.* silicotungstic, and phosphatotungstic acid, etc. M. Luckiesh [23] studied the tungsten filament lamp in therapeutics. Tungsten oxide, and tungstates have been used in dyeing ; [24] as a mordant [25] for rendering textile fabrics non-inflammable ; as a pigment [26]—*e.g.* the blue oxide forms the so-called *mineral blue* or *blue carmine ;* the trioxide, *mineral yellow ;* copper and chromium tungstates ; and the group of complex tungstates of the alkalies and alkaline earths known as *tungsten bronzes ;* and for pottery and glass colours.[27]

References.

[1] B. Thiede, *Ueber die Hydride der Metalle Nickel, Cobalt, Eisen, Chrom*, Berlin, 1926 ; T. Wiechselfelder and B. Thiede, *Liebig's Ann.*, **447**. 64, 1926 ; M. A. Schirmann, *Phys. Zeit.*, **27**. 748, 1926 ; H. Möhl, *Ueber die Reduktion von schwerschmelzbaren Oxyden in Gegenwart von Wolfram bei hohen Temperaturen und ein neues Mikropyrometer*, Leipzig, 1927 ; H. von Wartenberg and H. Möhl, *Zeit. phys. Chem.*, **128**. 439, 1927 ; O. Schmidt, *ib.*, **118**. 193, 1925 ; A. Sieverts and E. Bergner, *Ber.*, **44**. 2394, 1911 ; S. Hilpert and M. Ornstein, *ib.*, **46**. 1669, 1913 ; M. le Blanc, and O. Weyl, *ib.*, **45**. 2300, 1912 ; L. von Uslar, *Gött. Nachr.*, **94**. 255, 1855 ; *Beiträge zur Kenntniss des Wolframs und Molybdäns*, Göttingen, 1855 ; J. J. and F. de Elhuyar, *Análisis quimico del volfram y exámen de un nuovo metal que entra en su compisicion*, Bascongada, 1783 ; *A Chemical Examination of Wolfram and Examination of a New Metal which enters into its Composition*, London, 1785 ; *Chemische Zerkliederung des Wolframs*, Halle, 1786 ; *Mém. Acad. Toulouse*, **2**. 141, 1784 ; F. Fischer and F. Schrötter, *Ber.*, **43**. 1442, 1910 ; A. Riche, *Ann. Chim. Phys.*, (3), **50**. 33, 1857 ; H. Moissan, *ib.*, (7), **8**. 570, 1896 ; *Le four électrique*, Paris, 229, 1897 ; London, 159, 1904 ; *Compt. Rend.*, **73**. 13, 1872 ; **116**. 1225, 1893 ; **123**. 13, 1896 ; E. Zettnow, *Pogg. Ann.*, **130**. 16, 241, 1867 ; E. R. Schneider, *Pogg. Ann.*, **93**. 474, 1854 ; *Journ. prakt. Chem.*, (1), **50**. 154,

321, 1850 ; H. E. Roscoe, *Liebig's Ann.*, **162**. 359, 1872 ; *Proc. Manchester Lit. Phil. Soc.*, **11**. 79, 1872 ; *Chem. News*, **25**. 61, 73, 90, 1873 ; *Bull. Soc. Chim.*, (2), **25**. 61, 1873 ; L. A. Hallopeau, *ib.*, (3), **19**. 997, 1898 ; (3), **21**. 266, 1899 ; *Ann. Chim. Phys.*, (7), **19**. 115, 1900 ; *Compt. Rend.*, **127**. 755, 1899 ; S. M. Delépine and L. A. Hallopeau, *ib.*, **129**. 600, 1899 ; A. Stavenhagen, *ib.*, **127**. 755, 1899 ; *Ber.*, **32**. 1513, 3064, 1899 ; J. B. von Borck, *Journ. prakt. Chem.*, **54**. 254, 1851 ; *Oefvers Akad. Förh.*, **8**. 147, 1851 ; C. H. Ehrenfeld, *Journ. Amer. Chem. Soc.*, **17**. 381, 1895 ; E. D. Desi, *ib.*, **19**. 213, 1897 ; J. H. Muller, *ib.*, **33**. 1506, 1911 ; J. S. de Benneville, *ib.*, **16**. 648, 1894 ; W. E. Ruder, *ib.*, **34**. 387, 1912 ; I. Langmuir, *ib.*, **34**. 1310, 1912 ; **35**. 105, 1913 ; **37**. 1139, 1915 ; **41**. 167, 1919 ; *Trans. Faraday Soc.*, **17**. 607, 1921 ; *Gen. Elect. Rev.*, **29**. 153, 1926 ; *Phys. Zeit.*, **14**. 1373, 1913 ; J. Férée, *Bull. Soc. Chim.*, (3), **19**. 213, 1898 ; A. Korczynsky, *ib.*, (4), **29**. 283, 1921 ; E. F. Smith, *Zeit. anorg. Chem.*, **1**. 360, 1892 ; L. Weiss, *ib.*, **65**. 279, 1910 ; E. F. Smith and V. Oberholtzer, *ib.*, **5**. 63, 1894 ; *Journ. Amer. Chem. Soc.*, **15**. 206, 1893 ; E. F. Smith and H. Fleck, *ib.*, **21**. 1008, 1899 ; F. W. Bergstrom, *ib.*, **47**. 1826, 1925 ; C. H. Kunsman, *ib.*, **50**. 2110, 1928 ; A. Westgren and G. Phragmen, *Zeit. anorg. Chem.*, **156**. 27, 1926 ; V. I. Spitzin and L. Kaschtanoff, *ib.*, **157**. 141, 1926 ; G. Tammann and K. Schönert, *ib.*, **122**. 27, 1922 ; R. E. Burk, *Proc. Nat. Acad.*, **14**. 601, 1928 ; E. Martin, *Arch. Eisenhüttenwesen*, **3**. 407, 1929 ; *Stahl Eisen*, **49**. 1681, 1929 ; *Ein Beitrag zur Frage der Aufnahmefähigkeit des reinen Eisens und einiger seiner Legierungselemente für Wasserstoff und Stickstoff*, Düsseldorf, 1929 ; C. G. Fink, *Trans. Amer. Electrochem. Soc.*, **22**. 499, 1912 ; *Met. Chem. Engg.*, **8**. 341, 1910 ; *Chem. News*, **104**. 34, 1911 ; M. R. Andrews and S. Dushman, *Journ. Franklin Inst.*, **192**. 545, 1921 ; *Journ. Phys. Chem.*, **29**. 462, 1925 ; M. R. Andrews, *ib.*, **27**. 270, 1923 ; Regina Bogenlampenfabrik, *German Pat.*, *D.R.P.* 228286, 1908 ; L. Wöhler and W. Prager, *Zeit. Elektrochem.*, **23**. 199, 1917 ; L. Wöhler and O. Balz, *ib.*, **27**. 406, 1921 ; O. Ruff, *ib.*, **30**. 356, 1924 ; Z. Jeffries and P. P. Tarasov, *Trans. Amer. Inst. Min. Met. Eng.—Min. Met.*, 1614, E, 1927 ; H. Davy, *Phil. Trans.*, **101**. 155, 1811 ; C. Matignon and G. Desplantes, *Compt. Rend.*, **140**. 853, 1905 ; M. Wunder and B. Janneret, *ib.*, **152**. 1770, 1911 ; C. Beindl, *U.S. Pat. No.* 1492193, 1492194, 1924 ; F. Emich, *Monatsh.*, **15**. 375, 1894 ; C. Zwikker, *Physica*, **7**. 189, 1927 ; F. Haber, *German Pat.*, *D.R.P.* 259996, 1913 ; E. J. B. Willey, *Journ. Chem. Soc.*, 2188, 1927 ; A. Burger, *Reduktion durch Calcium*, Basel, 17, 1907 ; C. W. Siemens and A. K. Huntington, *Chem. News*, **46**. 163, 1882 ; N. R. Campbell, *Phil. Mag.*, (7), **2**. 369, 1927 ; W. Rohn, *Zeit. Metallkunde*, **18**. 387, 1926 ; W. Guertler and T. Liepus, *ib.*, **17**. 310, 1925 ; W. Geiss and J. A. M. van Liempt, *ib.*, **16**. 317, 1924 ; R. H. Adie, *Proc. Chem. Soc.*, **15**. 133, 1899 ; *Chem. News*, **79**. 261, 1899 ; C. J. Smithells, *Trans. Faraday Soc.*, **17**. 485, 1921 ; *Journ. Chem. Soc.*, **121**. 2236, 1922 ; C. J. Smithells and H. P. Rooksby, *ib.*, 1882, 1927 ; C. N. Hinshelwood and C. R. Prichard, *ib.*, **127**. 1546, 1926 ; L. O. Bannister, *ib.*, 3163, 1928 ; *Metal Ind.*, **35**. 27, 1928 ; N. B. Pilling and R. E. Bedworth, *Chem. Trade Journ.*, **72**. 317, 1923 ; *Journ. Inst. Metals*, **29**. 529, 1923 ; *Metal Ind.*, **22**. 560, 586, 619, 1923 ; *Chem. Met. Engg.*, **27**. 72, 1922 ; H. Alterthum and R. Becker, *Zeit. tech. Physik*, **6**. 306, 1925 ; C. Kenty and L. A. Turner, *Phys. Rev.*, (2), **29**. 914, 1927 ; (2), **32**. 799, 1928 ; *Nature*, **120**. 332, 1927 ; W. Samter and K. Schröter, *Zeit. tech. Phys.*, **6**. 305, 1925 ; W. Reinders and A. W. Vervloet, *Rec. Trav. Chim. Pays-Bas*, **42**. 625, 1923 ; L. J. Thénard, *Traité de chimie*, Paris, **2**. 68, 1824 ; N. Domanicky, *Journ. Russ. Phys. Chem. Soc.*, **48**. 1724, 1916 ; I. Zschukoff, *Ann. Inst. Anal. Phys. Chim.*, **3**. 14, 1926 ; P. C. Allen and C. N. Hinshelwood, *Proc. Roy. Soc.*, **121**. A, 141, 1928 ; J. S. Dunn, *ib.*, **111**. A, 207, 1926 ; *Journ. Chem. Soc.*, 1149, 1929 ; B. S. Srikantan, *Journ. Indian Chem. Soc.*, **7**. 745, 1930 ; O. Ruff and H. Krug, *Zeit. anorg. Chem.*, **190**. 270, 1930 ; A. Lottermoser, *Zeit. Elektrochem.*, **35**. 610, 1929 ; G. Hägg, *Zeit. phys. Chem.*, **12**. B, 33, 1931 ; S. L. Malowan, *Zeit. Metallkunde*, **23**. 70, 1931 ; W. G. Burgers and J. A. M. van Liempt, *Zeit. anorg. Chem.*, **193**. 144, 1930 ; G. Agte and H. Alterthum, *Zeit. tech. Phys.*, **11**. 182, 1930 ; C. H. Kunsman, E. S. Lamar and W. E. Deming, *Phil. Mag.*, (7), **10**. 1015, 1930.

[2] C. G. Gmelin, *Schweigger's Journ.*, **43**. 110, 1835 ; *Edin. Journ. Med.*, **3**. 324, 1927.

[3] M. Barber, *Monatsh.*, **27**. 379, 1906 ; E. Kafka, *Zeit. anal. Chem.*, **51**. 482, 1912 ; E. Pozzi-Escot, *Bull. Soc. Chim.*, (4), **13**. 402, 1042, 1913 ; W. T. Taggart and E. F. Smith, *Journ. Amer. Chem. Soc.*. **18**. 1053, 1896 ; J. H. Muller, *ib.*, **33**. 1506, 1911 ; A. A. Noyes and W. C. Bray, *ib.*, **29**. 137, 1907 ; A. A. Noyes, *Tech. Quart.*, **19**. 191, 1906 ; *Chem. News*, **93**. 134, 1906 : G. Torossian, *Amer. Journ. Science*, (4), **38**. 537, 1914 ; M. L. Hartmann, *Pahasapa Quart.*, **5**. 23, 1916 ; *Min. Scient. Press*, **112**. 941, 1916 ; H. J. H. Fenton, *Journ. Chem. Soc.*, **93**. 1064, 1908 ; F. L. Hess, *Min. Science.*, **62**. 31, 1910 ; J. H. de Boer, *Chem. Weekbl.*, **21**. 404, 1924 ; E. Zettnow, *Pogg. Ann.*, **130**. 16, 241, 1867 ; E. F. Smith, *Proc. Amer. Phil. Soc.*, **65**. 10, 1926.

[4] W. D. Coolidge, *Proc. Amer. Inst. Elect. Eng.*, **31**. 1219, 1912 ; *Journ. Ind. Eng. Chem.*, **4**. 2, 1912 ; C. G. Fink, *ib.*, **10**. 580, 684, 1913 ; *Internat. Congr. Appl. Chem.*, **8**. 503, 1912 ; *Trans. Amer. Electrochem. Soc.*, **22**. 499, 1912 ; H. F. Baumhauer, *Bayr. Ind. Gewerbebl.*, 141, 1912 ; *Ind. Chem.*, **12**. 343, 1912 ; N. Branoic, *Giorn. Bibl. Tech. Internat.*, **1**. 3, 1925 ; R. P. Skinner, *Daily Consular Trade Rep.*, **15**. 793, 1913 ; Anon., *Chem. News*, **114**. 125, 1916 ; G. M. Dyson, *Chem. Age*, **16**. 33, 1927 ; W. C. Blake, *Journ. Western Soc. Eng.*, **27**. 223, 1922 ; *Journ. Ind. Eng. Chem.*, **21**. 1002, 1929 ; H. Lohmann, *Electrochem. Zeit.*, **25**. 141, 1919 ; J. L. F. Vogel, *Mining Mag.*, **20**. 12, 1919 ; R. Cazaud, *Aciers Spéciaux*, **5**. 423, 1930.

[5] S. Chapman and W. W. Bryant, *Nature*, **92**. 585, 1914 ; G. W. Sears, *School Science*, **18**. 145, 1918 ; Anon., *Chem. Trade Journ.*, **69**. 821, 1921.

[6] E. Haynes, *Journ. Ind. Eng. Chem.*, **5**. 189, 1913 ; *Eng. Min. Journ.*, **105**. 997, 1918 ; *Trans. Amer. Inst. Min. Eng.*, **44**. 573, 1913 ; **54**. 3, 1915 ; F. A. Fahrenwald, *ib.*, **54**. 541, 1916 ; *Journ. Nat. Dental. Assoc.*, **4**. 372, 1917 ; J. T. Bottomley, *Proc. Roy. Soc.*, **38**. 340, 1885 ;

E. Weintraub, *U.S. Pat. No.* 1096655, 1915; F. A. Bernoulli, *Pogg. Ann.*, **111**. 573, 1860; *Chem. News*, **5**. 116, 1862; J. G. Escard, *Le Génie Civil*, **55**. 74, 85, 1909; *Oesterr. Zeit. Berg. Hütt.*, **58**. 201, 1910; A. Hoenig, *ib.*, **56**. 177, 196, 208, 221, 1908; L. Weiss, *Zeit. anorg. Chem.*, **65**. 280, 1910; E. Groschuff and F. Mylius, *Zeit. Elektrochem.*, **21**. 286, 1915; P. Monnartz, *Met.*, **8**. 161, 193, 1911; H. Leiser, *Wolfram*, Halle, 1910; *Chem. Ztg.*, **35**. 665, 685, 702, 714, 1911; H. Mennicke, *Die Metallurgie des Wolframs*, Berlin, 1911; J. W. Richards, *Journ. Franklin Inst.*, **157**. 394, 1904; J. S. de Benneville, *Journ. Amer. Chem. Soc.*, **16**. 735, 1894; J. J. Runner and M. L. Hartmann, *The Occurrence, Chemistry, Metallurgy, and Uses of Tungsten*, Rapid City, 1918; H. Alterthum, *Zeit. angew. Chem.*, **42**. 275, 308, 1929.

[7] J. Trowbridge, and S. Sheldon, *Proc. Amer. Acad.*, **24**. 176, 1889; *Amer. Journ. Science*, (3), **39**. 462, 1889; *Chem. News*, **60**. 312, 1889.

[8] W. Fehse, *Elektrische Oefen mit Heizkörpern aus Wolfram*, Braunschweig, 1928.

[9] G. M. J. Mackay and C. V. Ferguson, *Journ. Franklin Inst.*, **181**. 209, 1916; B. H. Morphy and S. R. Millard, *Journ. Roentgen Soc.*, **12**. 70, 1916; M. Wilson, *ib.*, **12**. 83, 1916.

[10] C. Limb, *Compt. Rend.*, **152**. 252, 1911; *L'Ind. Elect.*, **20**. 120, 1911.

[11] F. Fischer and E. Tiede, *Ber.*, **44**. 171, 1911; A. H. Compton, *Journ. Amer. Opt. Soc.*, **6**. 910, 1922; F. A. Fahrenwald, *Journ. Ind. Eng. Chem.*, **8**. 436, 1916.

[12] H. Alterthum, *Zeit. angew. Chem.*, **42**. 275, 308, 1923.

[13] R. Eisenmann, *Dingler's Journ.*, **263**. 540, 1887.

[14] J. H. Robertson and D. Jankower, *U.S. Pat. No.* 1333036, 1920; J. Harden, *Chem. Met. Engg.*, **33**. 543, 1926.

[15] W. D. Coolidge, *Proc. Amer. Inst. Elect. Eng.*, **31**. 1219, 1912; *Phys. Rev.*, (2), **2**. 409, 1912; *Engg.*, **110**. 119, 1920; *Met. Chem. Engg.*, **10**. 146, 1913; J. H. Gardner, *Nature*, **97**. 67, 1916; R. Jacoby, *U.S. Pat. No.* 1648690, 1927.

[16] R. Kruger, *München. Med. Wochenschr.*, **59**. 1910, 1913.

[17] H. Alterthum, *Zeit. angew. Chem.*, **42**. 275, 308, 1923.

[18] F. Haber, *German Pat., D.R.P.* 259996, 1913; C. Beindl, *U.S. Pat. No.* 1492193, 1492194, 1924.

[19] C. N. Hinshelwood and C. R. Prichard, *Journ. Chem. Soc.*, **127**. 1546, 1925.

[20] P. Sabatier, *Chem. Ztg.*, **50**. 802, 1926.

[21] A. Kurtenacker, *Zeit. anal. Chem.*, **50**. 548, 1911.

[22] F. A. Gooch and S. B. Kuzirian, *Amer. Journ. Science*, (4), **31**. 497, 1911; *Zeit. anorg. Chem.*, **71**. 323, 1911; G. H. Nievenglowsky, *Jahrb. Phot.*, **9**. 24, 1895; E. Wörner, *Ber. deut. pharm. Ges.*, **10**. 4, 1900; G. C. Meyer, *Chem. Ztg.*, **31**. 158, 1907; G. Bertrand, *Compt. Rend.*, **128**. 742, 1899; C. Frabot, *Ann. Chim. Anal. Appl.*, **9**. 371, 1899; H. Moreigne, *ib.*, **10**. 15, 1905; M. Javillier and B. Guérithault, *Bull. Soc. Pharmacol.*, **18**. 93, 1911; W. A. Ross, *Chem. News*, **41**. 187, 1880; A. Werner, *Pharm. Centrh.*, **30**. 515, 1889; F. Mylius, *Ber.*, **36**. 775, 1903; W. Stahl, *ib.*, **25**. 1600, 1892; E. Schär, *Arch. Pharm.*, **232**. 249, 1896; F. A. McDermott, *Journ. Amer. Chem. Soc.* **33**. 410, 1911; R. D. Hall and E. F. Smith, *Proc. Amer. Phil. Soc.*, **44**. 196, 1905; O. Folin and D. Denis, *Journ. Biol. Chem.*, **12**. 239, 1914; O. Folin and A. B. Macallum, *ib.*, **11**. 265, 1913.

[23] A. Luckiesh, *Journ. Franklin Inst.*, **206**. 57, 1928.

[24] Société Scheurer et Lauth, *French Pat. No.* 253741, 1896; *Monit. Scient.*, (4), **10**. 189, 1896; A. Scheurer, *Chem. Ztg.*, **25**. 273, 1902.

[25] F. Versmann and A. Oppenheim, *On Rendering Fabrics Non-inflammable*, London, 1859; *B.A. Rep.*, 86, 1859; *Pharm. Journ.*, (2), **1**. 385, 422, 1860.

[26] C. A. F. Kahlbaum, *German Pat., D.R.P.* 91605, 1896; *Zeit. angew. Chem.*, **10**. 290, 1897; M. Sacc, *Les Mondes*, **19**. 230, 1844; E. F. Anthon, *Bibl. Univ.*, **13**. 202, 1838; *Journ. prakt. Chem.*, (1), **9**. 8, 1836.

[27] A. Granger, *Bull. Soc. Chim.*, (3), **19**. 793, 1898; *Compt. Rend.*, **127**. 106, 1898; **140**. 935, 1905; M. Hertwig, *Ker. Rund.*, **18**. 105, 1910; K. Fuwa, *Journ. Japan. Cer. Assoc.*, 370, 1923.

§ 7. The Atomic Weight and Valency of Tungsten

There is a close relationship between the valencies of chromium, molybdenum, and tungsten. Tungsten appears to be *bivalent* in the halides WCl_2, WBr_2, and WI_2, but the mol. wt. of these salts has not been determined. The observations of R. F. Bernhardi-Grisson [1] on the electrolytic reduction of tungstic acid, and of O. Olsson, and others on the complex chlorides, show that compounds with *tervalent* tungsten have probably been formed. The existence of the tetrahalides—WCl_4 and WI_4—as well as of the disulphide shows that *quadrivalent* tungsten can exist, although not established by mol. wt. determinations. A number of well characterized compounds of *quinquevalent* tungsten has been prepared, and the results have been confirmed by vapour density determinations by H. E. Roscoe, and H. Debray. O. Ruff and F. Eisner's hexafluoride shows that tungsten can also behave as a *sexivalent* element. This is confirmed by the existence of the hexachloride, oxyhalides, and the trioxide. N. V. Sidgwick discussed the co-valency of tungsten. The salts of pertungstic acid, HWO_4, or $HO.WO_3$, prepared by E. Péchard show that septivalent tungsten may exist.

Tungsten compounds were analyzed by M. H. Klaproth,[2] C. F. Bucholz, and J. J. and F. de Elhuyar, and the results led J. J. Berzelius to infer that the sulphide has the mol. ratio $W : S = 1 : 2$, and tungstic anhydride, $W : O = 1 : 3$. He added: "Tungsten and molybdenum form a similar series of oxides, and in its normal salts the acid anhydride contains three atoms of oxygen to one atom of oxygen in the base. The tungstates are also isomorphous with the molybdates indicating that the internal constitution is the same." This hypothesis makes the at. wt. of tungsten approximate 184. This is in agreement (i) with the vap. density determination of H. Debray, and O. Ruff and F. Eisner, and not in agreement with J. Persoz's assumption that the tungsten is quinquevalent in tungstic acid. (ii) It agrees with the at. ht. determinations of P. Nordmeyer and A. L. Bernoulli, of A. W. Grodspeed and E. F. Smith, and of E. Defacqz and M. Guichard. (iii) It is in accord with the isomorphism between the tungstates and molybdates observed J. J. Berzelius, and R. Funk. (iv) It is in harmony with the electrochemical eq. observed by M. Leblanc and H. G. Byers, E. F. Smith, A. Rosenheim and E. Dehn, and W. E. Koerner. (v) It is also in accord with the at. number, and the high frequency spectrum of H. G. J. Moseley. (vi) It agrees with the position of tungsten in the periodic table as a number of the chromium family. J. N. Frers discussed the place of tungsten in the periodic table.

The observations of F. J. Malaguti, F. Wöhler, A. Riche, H. V. Regnault, and J. C. G. de Marignac are not suited for fixing a value for the at. wt. of tungsten. General reviews of the at. wt. of tungsten were made by L. Meyer and K. Seubert, W. Ostwald, F. W. Clarke, and J. Meyer. The determinations include: (i) A series, based on the ratio $WO_3 : W$ obtained by reducing the trioxide to the metal, includes that of J. J. Berzelius, 188; E. R. Schneider, 184·2, and later, 184·0; R. F. Marchand, 183·9; J. B. von Borck, 183·7; J. B. A. Dumas, 184·0; F. A. Bernoulli, 184; J. Persoz, 184; H. E. Roscoe, 183·5; and J. Waddell, 184·3. (2) Another series, based on the ratio $W : WO_3$ obtained by oxidizing the metal to the trioxide, includes that of E. R. Schneider, 183·9; R. F. Marchand, 184·3; J. B. von Borck, 184·4; F. A. Bernoulli, 187; H. E. Roscoe, 183·5; M. E. Pennington and E. F. Smith, 184·9; O. L. Shinn, 184·0; E. F. Smith and W. L. Hardin, 184·1 to 184·8; and E. F. Smith and F. F. Exner, 184·07. (3) A series, based on the loss of water by tungstic acid involving the ratio $WO_3 : 3H_2O$, gave F. A. Bernoulli 186·62; and E. F. Smith and E. D. Desi, 184·7. (4) A series, based on the dehydration of barium metatungstate involving the ratio $BaW_4O_{13}.9H_2O : 9H_2O$, gave C. Scheibler 184·0. E. F. Smith and W. L. Hardin discussed these results. (5) H. E. Roscoe obtained 184·1 from the ratio $WCl_6 : 6AgCl$, and 183·9 from the ratio $WCl_6 : W$. (6) E. F. Smith and F. F. Exner obtained 184·10 from the ratio $WCl_6 : WO_3$. (7) E. Zettnow analyzed ferrous tungstate and obtained 183·6 from the ratio $FeWO_4 : FeO$. (8) The analyses of silver tungstate furnished E. Zettnow with the value 183·6 from the ratio $Ag_2WO_4 : Ag_2O$, and also from the ratio $Ag_2WO_4 : 2AgCl$. (9) T. M. Taylor measured the carbon dioxide displaced by tungstic acid from carbonates and obtained 183·5 from the ratio $WO_3 : CO_2$, and likewise E. F. Smith and F. F. Exner obtained 183·6. (10) G. E. Thomas obtained 184·7 by measuring the water of crystallization in sodium tungstate. F. W. Clarke's general review gave 184·575 for the best representative value; and J. Meyer's, 184·1. The International Table for 1929 gave 184.

The **atomic number** of tungsten is 74. F. W. Aston[3] found that tungsten has four **isotopes** with the respective mass numbers 182, 183, 184, and 186; and the respective percentage abundances 22·6, 17·2, 30·1, and 30·0 per cent. The corresponding at. wt. is 183·96 in agreement with the representative value 184 now employed. The isotopic form reported by M. Gerber, was rendered improbable by the negative results of P. Barbe. N. Bohr's view of the **electronic structure** is symbolized: (2) for the K-shell; (4,4) for the L-shell; (6,6,6) for the M-shell; (8,8,8,8) for the N-shell; (4,4,4) for the O-shell; and (2) for the P-shell. The subject was discussed by E. C. Stoner, A. Dauvillier, O. Feussner, H. G. Grimm, J. D. M. Smith, and C. D. Niven. Neither E. Rutherford and J. Chadwick, nor H. Pettersson and G. Kirsch, reported any observations on the **atomic disruption** of tungsten when bombarded by α-rays. The subject was discussed by G. I. Podrowsky.

G. L. Wendt and C. E. Irion attempted to decompose tungsten by rapidly discharging a condenser holding 30,000 to 45,000 volts through a tungsten wire 4 cm. long and 0·035 mm. diam., either in vacuo or in carbon dioxide at 1 atm. press. In this way, a momentary temp. above 20,000° was produced in the wires, which were entirely dissipated, no smoke, dust or solid residue being found after the explosion. Abundant quantities of gas were present after the explosions in vacuo, and a spectroscopic examination of this showed the strong yellow helium line, and two red, one bright blue, and one pale violet line was also observed but have not been identified. About the same weight (mean 0·173 mg.) of tungsten furnished from 3·62 to 0·30 c.c. of gas unabsorbable by potassium hydroxide. If the whole of the tungsten had been decomposed into helium the volume of gas would have been 4·0 c.c. The results were questioned by D. M. Goetschius, and attempts to verify the observations by H. V. A. Briscoe and co-workers, S. Smith, and W. D. Harkins and S. K. Allison showed that G. L. Wendt and C. E. Irion's statements are based on erroneous observations. L. Thomassen observed no sign of change in an X-ray tube after the tungsten had been bombarded 90 hrs.

REFERENCES.

[1] R. F. Bernhardi-Grisson, *Die kathodische Reduktion der Wolframsäure*, Berlin, 1910; A. Rosenheim and R. F. Bernhardi-Grisson, *Ber. Internat. Cong. Appl. Chem.*, **7**. x, 120, 1911; O. Olsson, *Ber.*, **46**. 566, 1913; H. Debray, *Compt. Rend.*, **60**. 820, 1865; E. Péchard, *ib.*, **112**. 1060, 1891; H. E. Roscoe, *Liebig's Ann.*, **162**. 359, 1872; *Proc. Manchester Lit. Phil. Soc.*, **11**. 79, 1872; *Chem. News*, **25**. 61, 73, 90, 1873; *Bull. Soc. Chim.*, (2), **25**. 61, 1873; O. Ruff and F. Eisner, *Ber.*, **38**. 742, 1905; **40**. 2926, 1907; *Zeit. anorg. Chem.*, **52**. 256, 1907; N. V. Sidgwick, *Journ. Chem. Soc.*, **125**. 2672, 1924.

[2] M. H. Klaproth, *Beiträge zur chemischen Kenntnis der Mineralkörper*, Berlin, **3**. 47, 1802; J. J. and F. de Elhuyar, *Análisis quimico del volfram y exámen de un nuovo metal que entra en su composicion*, Bascongada, 1783; *A Chemical Examination of Wolfram and Examination of a New Metal which enters into its Composition*, London, 1785; *Chemische Zerkliederung des Wolframs*, Halle, 1786; *Mém. Acad. Toulouse*, **2**. 141, 1784; C. F. Bucholz, *Schweigger's Journ.*, **3**. 1, 1811; J. J. Berzelius, *Lehrbuch der Chemie*, Dresden, **3**. 1209, 1845; *Afhand. Fys. Kemi Min.*, **5**. 484, 1818; *Gilbert's Ann.*, **38**. 216, 1811; *Pogg. Ann.*, **4**. 151, 1825; **8**. 73, 1826; E. Zettnow, *ib.*, **130**. 45, 1867; F. A. Bernoulli, *ib.*, **111**. 573, 1860; *Chem. News*. **5**, 116, 1862; F. J. Malaguti, *Ann. Chim. Phys.*, (2), **60**. 271, 1835; A. Riche, *ib.*, (3), **50**. 10, 1857; *Compt. Rend.*, **42**. 203, 1856; H. Debray, *ib.*, **40**. 1098, 1855; **60**. 820, 1865; E. F. Smith, *Monograph on Atomic Weights*, Pennsylvania, 1915; *Zeit. anorg. Chem.*, **1**. 360, 1892; M. E. Pennington and E. F. Smith, *Proc. Amer. Phil. Soc.*, **33**. 332, 1894; *Zeit. anorg. Chem.*, **8**. 198, 1895; A. W. Grodspeed and E. F. Smith, *ib.*, **8**. 207, 1895; E. F. Smith and E. D. Desi, *ib.*, **8**. 205, 1895; *Proc. Amer. Phil. Soc.*, **33**. 337, 1894; E. F. Smith and F. F. Exner, *ib.*, **43**. 123, 1904; *Chem. News*, **90**. 37, 49, 66, 1904; *Journ. Amer. Chem. Soc.*, **26**. 1082, 1904; G. E. Thomas, *ib.*, **21**. 373, 1017, 1899; *The Atomic Mass of Tungsten and the Preparation of Sodium Pertungstate by means of the Electric Current*, Philadelphia, 1898; O. L. Shinn, *The Atomic Mass of Tungsten*, Philadelphia, 1896; *Journ. Amer. Chem. Soc.*, **19**. 359, 1897; W. L. Hardin, *ib.*, **19**. 657, 1897; E. F. Smith and W. L. Hardin, *ib.*, **21**. 1007, 1899; T. M. Taylor, *ib.*, **24**. 629, 1902; *The Atomic Weight of Tungsten; and the Ammonium Tungstates*, Philadelphia, 1901; E. R. Schneider, *Pogg. Ann.*, **93**. 474, 1854; *Journ. prakt. Chem.*, (1). **50**. 152 1850; (2), **53**. 288, 1896; C. Scheibler, *ib.*, (1), **83**. 324, 1861; J. B. von Borck, *ib.*, (1), **54**. 254, 1851; *Oefvers. Akad. Förh.*, **8**. 147, 1851; R. F. Marchand, *Liebig's Ann.*, **77**. 261, 1851; H. E. Roscoe, *ib.*, **162**. 359, 1872; *Proc. Manchester Lit. Phil. Soc.*, **11**. 79, 1872; *Bull. Soc. Chim.*, (2), **25**. 61, 1873; *Chem. News*. **25**. 61, 73, 1873; J. Waddell, *Amer. Chem. Journ.*, **8**. 280, 1886; *Chem. News*, **55**. 101, 112, 1887; *Trans. Roy. Soc. Edin.*, **33**. 1, 1889; *Zeit. phys. Chem.*, **3**. 491, 1889; J. B. A. Dumas, *Ann. Chim. Phys.*, (3), **55**. 143, 1859; E. Defacqz and M. Guichard, *ib.*, (7), **24**. 139, 1901; H. V. Regnault, *ib.*, (4), **3**. 71, 1864; J. C. G. de Marignac, *ib.*, (4), **3**. 66, 1864; J. Persoz, *ib.*, (4), **1**. 93, 1864; *Bull. Soc. Chim.*, (2), **2**. 188, 1864; O. Ruff and F. Eisner, *Ber.*, **38**. 742, 1905; A. Rosenheim and E. Dehn, *ib.*, **48**. 1167, 1915; R. Funk, *ib.*, **33**. 3696, 1900; P. Nordmeyer and A. L. Bernoulli, *Ber. deut. phys. Ges.*, **5**. 175, 1907; M. Leblanc and H. G. Byers, *Zeit. phys. Chem.*, **69**. 13, 1909;

F. Wöhler, *Pogg. Ann.*, **2**. 345, 1824; *Gött. Nachr.*, 35, 1850; *Liebig's Ann.*, **73**. 190, 1850; **77**. 262, 1851; *Ann. Chim. Phys.*, (2), **29**. 43, 1823; F. W. Clarke, *A Recalculation of the Atomic Weights*, Washington 359, 1910; W. E. Koerner, *Met. Chem. Engg.*, **15**. 522, 1916; **16**. 40, 1917; *Trans. Amer. Electrochem. Soc.*, **30**. 222, 1916; **31**. 221, 1917; H. G. J. Moseley, *Phil. Mag.*, (6), **27**. 703, 1914; L. Meyer and K. Seubert, *Die Atomgewichte der Elemente*, Leipzig, 188, 1883; W. Ostwald, *Lehrbuch der allgemeinen Chemie*, Leipzig, **1**. 120, 1903; J. Meyer in R. Abegg, *Handbuch der anorganischen Chemie*, Leipzig, **4**. i (2), 702, 1921; J. W. Frers, *Zeit. anorg. Chem.*, **186**. 145, 1930.

[3] F. W. Aston, *Proc. Roy. Soc.*, **115**. A, 487, 1927; *Nature*, **126**. 913, 1930; *Phil. Mag.*, (6), **49**. 1191, 1925; E. C. Stoner, *ib.*, (6), **48**. 719, 1924; C. D. Niven, *ib.*, (7), **3**. 1314, 1927; H. G. Grimm, *Zeit. phys. Chem.*, **101**. 403, 1922; M. Gerber, *Monit. Scient.*, (5), **7**. 73, 121, 169, 219, 1917; P. Barbe, *ib.*, (5), **9**. 73, 1919; N. Bohr, *Nature*, **112**. Suppl., 1923; E. Rutherford and J. Chadwick, *Proc. Phys. Soc.*, **36**. 417, 1925; *Nature*, **113**. 457, 1924; H. Pettersson and G. Kirsch, *Sitzber. Akad. Wien*, **134**. 491, 1925; *Atomzertrümmerung*, Leipzig, 1926; D. M. Goetschius, *Chem. Met. Engg.*, **26**. 676, 1922; G. L. Wendt, *ib.*, **26**. 772, 1922; *Science*, (2), **55**. 567, 1922; G. L. Wendt and C. E. Irion, *Chem. Met. Engg.*, **26**. 567, 1922; *Journ. Amer. Chem. Soc.*, **44**. 1887, 1922; W. D. Harkins and S. K. Allison, *ib.*, **46**. 814, 1924; S. Smith, *Proc. Nat. Acad.*, **10**. 4, 1924; H. V. A. Briscoe, P. L. Robinson, and G. E. Stephenson, *Journ. Chem. Soc.*, **127**. 240, 1925; O. Feussner, *Zeit. Physik*, **25**. 215, 1924; G. I. Podrowsky, *ib.*, **57**. 560, 1929; **63**. 561, 1930; A. Dauvillier, *Compt. Rend.*, **173**. 647, 1921; L. Thomassen, *Phys. Rev.*, (2), **33**. 229, 1929; *Metallwirtschaft*, **7**. 703, 1928; J. D. M. Smith, *Journ. Chem. Soc.*, 2029, 1927.

§ 8. Alloys and Intermetallic Compounds of Tungsten

Alloys of **copper** and tungsten were prepared by J. J. and F. de Elhuyar,[1] and F. A. Bernoulli obtained them by the simultaneous reduction of both metals. The alloys were said to be difficult to melt. J. Percy hoped that alloys with tungsten might be hard, and resist oxidation, but on trial, the results were unsatisfactory. C. L. Sargent obtained the alloy by reducing the mixed oxides with sugar charcoal in the electric arc furnace; and E. W. von Siemens and J. G. Halske reduced copper tungstate by hydrogen. C. Liebenoff obtained the alloys by dipping a lead plate in a soln. of copper and tungsten in dil. sulphuric acid. The brownish-red metals are ductile. When heated electrically in vacuo, the copper distils off. T. Kniesche, and E. W. L. Biermann, and P. Berthier reported alloys with 10 per cent. tungsten. D. Kremer, and H. List added that copper does not form homogeneous alloys with tungsten. O. Rumschöttel tried to make alloys by the simultaneous reduction of copper and tungsten oxides by the aluminothermite process; but found that as the molten alloy cools, the tungsten separates out. He also found that the tungsten separates from ternary alloys of tungsten, copper, and aluminium, nickel, or cobalt; similar results were obtained with quaternary alloys of tungsten, copper, and zinc with iron, cobalt, or nickel. J. G. Escard studied the tungsten-copper alloys. H. List said that a satisfactory regulus can be obtained only in the presence of a third element, say, silicon; the resulting ternary alloy is golden-yellow, and tough.

J. J. and F. de Elhuyar prepared alloys of **silver** and tungsten, which they said were pale brown, spongy, and malleable. F. A. Bernoulli was not able to alloy these metals. E. F. Smith said that when tungsten is placed in an ammoniacal soln. of silver nitrate, the silver is quantitatively precipitated. J. J. and F. de Elhuyar also obtained an alloy with **gold** which they described as being yellow and difficult to melt. G. Fuchs said that before alloying silver or gold with tungsten one of the metals is first alloyed with nickel, iron, or aluminium. A gold alloy containing 75 parts of gold to 10 to 15 of tungsten and 10 to 15 parts of nickel, may be used in jewellery as a substitute for platinum. It can be cast, hammered, and rolled and takes a much finer polish than does platinum. An alloy of 80 parts of fine silver, 10 to 15 of nickel, is said to have a greater strength than the gold alloy. It is much less affected by atmospheric oxidation than silver and takes a better polish. These alloys may also find technical application on account of their resistance to acid attack.

F. Wirth mentioned the use of an alloy with **beryllium** as a hardening agent for the filaments of incandescent lamps. H. List was not able to obtain alloys either with **calcium** and tungsten or with **magnesium** and tungsten. J. J. and F. de Elhuyar, and F. A. Bernoulli obtained an alloy of **zinc** and tungsten by the simultaneous reduction of the mixed oxides. The alloy loses zinc when heated. H. List added that zinc does not alloy with tungsten. J. G. Escard studied the alloys of tungsten, copper and zinc. H. von Miller, and F. Jones discussed the action of tungsten on brass.

A. S. Russell and co-workers found that the solubility of tungsten in **mercury** is very small, being of the order of 10^{-5} grm. per gram of mercury. R. F. Bernhardi-Grisson, and G. Tammann and J. Hinnüber obtained **tungsten amalgam** by the electrolysis of a soln. of tungsten trioxide in alcoholic hydrochloric acid and a mercury cathode. The solubility of tungsten in mercury is less than that of molybdenum. J. Férée obtained the amalgam by the electrolysis of a soln. of tungstic acid in hydrochloric acid using a mercury cathode. A. S. Russell found that metals are removed from their amalgams by oxidizing agents in the order Zn, Mn, Cu, Cr, Fe, Mo, Co, Hg, Ni, W.

F. Wöhler and F. R. Michel melted a mixture of tungsten trioxide, cryolite, potassium sodium chloride, and **aluminium** (1 : 2 : 2 : 1), and removed the excess of aluminium from the cold regulus by hydrochloric acid. There remained rhombic, prismatic crystals of sp. gr. 5·58, which were hard, and brittle. Cold, conc. acids had no action on the alloy, but hot nitric acid forms tungsten trioxide; hot hydrochloric acid dissolves the alloy forming a deep brown soln. of a lower chloride. Hot soda-lye removes all the aluminium leaving tungsten behind. H. Moissan, H. Schirmeister, J. W. Richards, and A. Stavenhagen prepared alloys of the metal; H. List said that the mixed metals do not form a homogeneous alloy, but in the presence of a third metal—cobalt, nickel, iron, or silicon—homogeneous alloys may be formed. Some tungsten separates from the ternary alloys of tungsten and aluminium with cobalt, iron, or silicon. L. Guillet studied the alloys in some detail, but without reference to the equilibrium diagram. He obtained them by igniting mixtures of aluminium and tungsten trioxide by a mixture of aluminium and 80 per cent. of barium dioxide. The alloys have a crystal structure. They are not attacked by oxygen at ordinary temp. or below a red-heat, but at a red-heat, tungsten trioxide, the blue oxide, and alumina are formed. Boiling water acts slowly, and the metal acquires a protective film of oxide. Chlorine has no action at ordinary temp., but at about 300°, volatile aluminium trichloride and tungsten hexachloride are formed. Hydrochloric acid acts slowly, but the Al_4W alloy is vigorously attacked by the boiling acid. Sulphuric acid acts slowly; and conc. boiling nitric acid slowly forms tungsten trioxide which is reduced to the blue oxide by the aluminium, and then oxidized to the trioxide once more. Potash-lye does not decompose the cold alloy, but when hot, there is a rapid attack which is more vigorous, the greater the proportion of contained aluminium. L. Guillet obtained what he regarded as **aluminium ditungstide,** AlW_2, from a mixture of tungsten trioxide and aluminium in the mol. proportions $Al : W_5$. The sp. gr. of the black, crystalline powder is 12·75 at 20°—the mixture rule gives a sp. gr. of 13·06. It is not attacked by aqua regia. A mixture of tungsten trioxide and aluminium in the mol. proportions $Al : W_4$ furnished **aluminium tritatungstide,** Al_3W, in quadratic prisms of sp. gr. 6·31 at 20°—theoretical value, 6·38. It is slowly decomposed by aqua regia. Similarly, tungsten trioxide and aluminium in the mol proportions $Al_4 : W$, gave lamellar crystals of **aluminium tetritatungstide,** Al_4W, of sp. gr. 5·56 at 20°—theoretical 5·62. The alloy is quickly decomposed by aqua regia. W. Campbell and J. A. Mathews obtained an alloy corresponding with Al_8W in thin monoclinic crystals readily attacked by aqua regia; and one with hexagonal crystals of Al_7W, which is not affected by aqua regia, and is slowly attacked by a fused mixture of alkali carbonate and nitrate. A. von Zeerleder studied the resistance of the Al–W alloys to acids. D. A. Roche prepared W–Al–Sb alloys; M. R. Whitmore and F. T. Sisco, R. L. Roman, C. Berg, G. Roman, and R. Wallace, W–Al–Cu alloys. The term *wolframinum* is a trade-name for one of the ternary alloys; and *partinium*, for an alloy of aluminium, copper, tin, antimony, and tungsten.

H. List said that tungsten does not alloy with **tin,** but J. J. and F. de Elhuyar described the alloy, and R. L. Roman, R. B. Wheatley, and the Hannoversch Industriegesellschaft prepared alloys of tin and tungsten with other metals. J. G. Escard studied the W–Sn–Cu alloys. H. von Miller, R. B. Wheatley, and J. Webster discussed the effect of tungsten on the copper-tin bronzes. H. List, and F. A. Bernoulli could not prepare alloys with **lead** by the direct union of the metals. J. J. and F. de Elhuyar reduced a mixture of tungsten trioxide with lead in a carbon crucible; F. A. Bernoulli used a mixture of lead oxide and tungsten trioxide; and A. Stavenhagen and E. Schuchard, a mixture of tungsten trioxide, lead oxide, and aluminium powder. The alloys were also prepared by H. Falkenberg, H. Kuzel, and H. Lieber. S. Inouye prepared alloys with up to 30 per cent. of tungsten. The thermal diagram is shown in Fig. 20. At 1300°, lead dissolves a maximum of 30 per cent. of tungsten. The temp. of primary crystallization could not be detected with less than 5 per cent. of tungsten. Tungsten crystallizes first, and the eutectic appears to be almost pure lead. No evidence of the formation of a compound on the lead side could be found, and it is improbable that there could be one on the tungsten side, on account of the low b.p. of lead. H. Falkenberg, and L. F. von Grotthuss-Call alloyed tungsten with lead and antimony for use as a bearing metal. L. Freiherr prepared ductile alloys of **thorium** and tungsten by reducing a mixture of thoria and tungsten trioxide—*vide supra*, ductile tungsten. S. Dushman and I. Langmuir, and P. Clausing discussed the diffusion of thorium in tungsten; A. St. John observed no evidence of an alloy of tungsten and thorium in thoriated tungsten filaments.

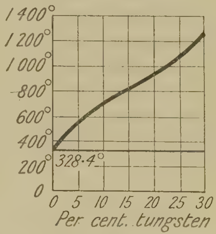


Fig. 20.—Freezing-point Curve of the Lead–Tungsten System.

F. A. Bernoulli, and C. L. Sargent obtained alloys with **antimony,** but not with **bismuth.** C. L. Sargent prepared alloys of tungsten and **chromium** by melting a mixture of the oxides and carbon in an electric furnace; and T. Goldschmidt obtained them by the aluminothermite process. E. Haynes also found that tungsten alloys with chromium and cobalt in all proportions. F. A. Fahrenwald, E. C. Bain, and Z. Jeffries prepared alloys of **molybdenum** and tungsten by compressing the reduced powders into briquettes, and heating them with an electric current in an atm. of hydrogen; and A. Stavenhagen and E. Schuchard, by the thermite process. W. Geiss and J. A. M. van Liempt observed no diffusion between the two metals in hydrogen at 2400° during 2 hrs., but with a pressed bar, diffusion occurs in 15 min. at this temp. H. Mennicke said that the compound *tungsten hemitrimolybdide*, W_2Mo_3, is formed by reducing molybdenum oxide with tungsten hemitrisilicide in the presence of lime: $W_2Si_3+3MoO_2+3CaO=3CaSiO_3+W_2Mo_3$. The silver-white crystals have a sp. gr. 14·8. A. Stavenhagen and E. Schuchard, and H. Mennicke said that *tungsten molybdide*, WMo, is formed by the aluminothermite process: $WO_3+MoO_3+4Al=2Al_2O_3+WMo$. There is not sufficient evidence to establish either of these products as a chemical individual. The equilibrium diagram, Fig. 21, by F. A. Fahrenwald is approximately a straight line from the f.p. of molybdenum to that of tungsten. W. Geiss and J. A. M. van Liempt, and Z. Jeffries also obtained analogous diagrams. This shows that the metals are completely isomorphous. There is no evidence of chemical combination or of eutectics. The electrical resistance curves, and the curves for the hardness (Fig. 22) of the alloys, are typical of an uninterrupted series of solid soln. Curve *A*, Fig. 22, refers to the metal which has suffered a 60-per cent. reduction, and *B*, the compressed, heat-treated but unforged ingot. Both curves are smoothly convex, and are typical of an uninterrupted series of solid soln. The etching tests agree with the presence of cubic crystals. W. Geiss and

J. A. M. van Liempt studied the electrical resistance and found the results in agreement with the assumption that the alloys form a continuous series of solid soln. According to A. E. van Arkel, the X-radiogram of the 50–50-alloy corresponds with a cube-centred lattice showing that the atoms in the isomorphous crystals are arranged in a space-lattice with definite places for the components. D. Binnie found that the molybdenum-tungsten thermocouple has an e.m.f. of 7 to 8 millivolts per degree at 1500°, and 8 to 9 millivolts at 1600°; and he made high temp. pyrometers with the couples. A. Stavenhagen and E. Schuchard also studied the alloys of tungsten and molybdenum as well as those of W–Mo–Ti, and W–Mo–Cr–Co, and E. W. von Siemens and J. G. Halske, those of chromium and tungsten. According to J. A. M. van Liempt, the corrosion of the alloys by acids, and by water, in some cases, starts rapidly at a particular composition, whilst in others it increases continuously with increase in the percentage of molybdenum. Where a sharp corrosion limit is shown, it is not a constant, but depends on the nature of the reagent, the temperature, and usually also on the time of reaction. The positions of the resistance limits do not agree with G. Tammann's theory. The subject was discussed by G. Tammann. A. Stavenhegen and E. Schuchard obtained his alloys by the thermite process. According to P. Reinglass, tungsten alloys in all proportions with **tantalum**, but with more than 10 per cent. of tantalum, the alloys are hard and brittle; with smaller proportions of tantalum, the alloys may be drawn into wires 0·1 mm. diameter.

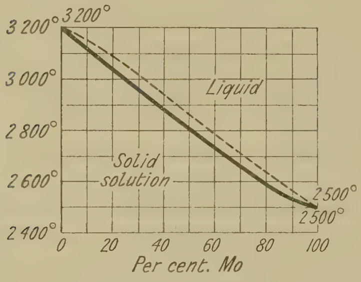


Fig. 21.—Freezing-point Curve of the Molybdenum–Tungsten System.

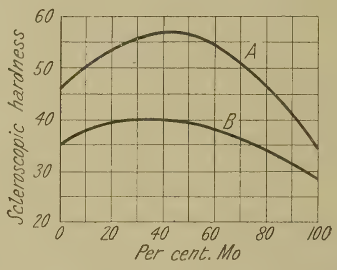


Fig. 22.—The Scleroscopic Hardness of the Molybdenum–Tungsten Alloys.

References.

[1] J. J. and F. de Elhuyar, *Análisis quimico del volfram y exámen de un nuovo metal que entra en su composicion*, Bascongada, 1783; *A Chemical Examination of Wolfram and Examination of a New Metal which enters into its Composition*, London, 1785; *Chemische Zerkliederung des Wolframs*, Halle, 1786; *Mém. Acad. Toulouse*, **2**. 141, 1784; F. A. Bernoulli, *Pogg. Ann.*, **111**. 573, 1860; *Chem. News*, **5**. 116, 1862; J. Percy, *Chem. Gaz.*, **6**. 349, 1858; C. L. Sargent, *Journ. Amer. Chem. Soc.*, **22**. 783, 1900; W. Campbell and J. A. Mathews, *ib.*, **24**. 253, 1902; E. W. von Siemens and J. G. Halske, *German Pat., D.R.P.* 201283, 1906; 419388, 1921; G. Fuchs, *ib.*, 304551, 1918; C. Liebenoff, *Zeit. Elektrochem.*, **4**. 227, 1897; E. F. Smith, *Zeit. anorg. Chem.*, **1**. 360, 1892; G. Tammann and J. Hinnüber, *ib.*, **160**. 249, 1927; L. Weiss, *ib.*, **65**. 279, 1910; G. Wirth, *ib.*, **79**. 359, 1913; G. Tammann, *ib.*, **169**. 151, 1928; H. List, *Edel.-Erden Erz*, **4**. 66, 1923; D. Kremer, *Beiträge zur Kenntnis des Wolframs*, Halle, 1915; D. Binnie, *Journ. Roy. Tech. Coll. Met. Club*, 6, 1928; P. Reinglass, *Chemische Technologie der Legierungen*, Leipzig, 463, 1919; A. von Zeerleder, *Metall Erz*, **14**. 325, 1917; K. Kreitz, *Kobalt-Wolfram-Legierungen*, Aachen, 1921; O. Rumschöttel, *Beiträge zur Frage der Löslichkeit von Wolfram in Kupfer*, Aachen, 1915; *Abhand. Inst. Metallhüttenwesen*, **1**. 19, 1915; *Metall Erz*, **12**. 45, 1915; L. F. von Grotthuss-Call, *ib.*, **10**. 844, 1913; T. Kniesch, *Stahl Eisen*, **6**. 627, 1886; H. Schirmeister, *ib.*, **35**. 649, 873, 996, 1915; *Beiträge zur Kenntnis der binären Aluminiumlegierungen hinsichtlich ihrer technischen Eigenschaften*, Düsseldorf, 1914; E. W. L. Biermann, *Berg. Hutt. Ztg.*, **33**. 268, 1874; J. Férée, *Bull. Soc. Chim.*, (3), **19**. 213, 1898; A. S. Russell and S. W. Rowell, *Journ. Chem. Soc.*, 1881, 1926; A. S. Russell, *ib.*, 2398, 1929; R. F. Bernhardi Grisson, *Die kathodische Reduktion der Wolframsäure*, Berlin, 1910; F. Wöhler and F. R. Michel, *Liebig's Ann.*, **115**. 102, 1860; F. R. Michel, *Ueber krystallisirte Verbindungen des Aluminiums*

mit Metallen, Göttingen, 1860; M. R. Whitmore and F. T. Sisco, *Journ. Ind. Eng. Chem.*, **17**. 15, 1925; P. Berthier, *Traité des essais par la voie sèche*, Paris, 2, 419, 1834; L. Guillet, *Bull. Soc. d'Enc. Nat. Ind.*, **101**. 222, 228, 1902; *La Génie Civil*, **41**. 363, 377, 393, 1902; *Compt. Rend.*, **132**. 1112, 1901; H. Moissan, *ib.*, **122**. 1302, 1896; *Bull. Soc. Chim.*, (3), **15**. 1282, 1896; *Ann. Chim. Phys.*, (8), **9**. 337, 1896; W. Geiss and J. A. M. van Liempt, *Zeit. Metallkunde*, **16**. 317, 1924; *Zeit. anorg. Chem.*, **128**, 355, 1923; J. A. M. van Liempt, *Rec. Trav. Chim. Pays-Bas*, **45**. 203, 1926; **46**. 11, 1927; J. W. Richards, *Journ. Franklin Inst.*, **157**. 394, 1904; A. Stavenhagen and E. Schuchard, *Ber.*, **35**. 909, 1902; A. Stavenhagen, *ib.*, **32**. 1513, 1899; S. Dushman and I. Langmuir, *Phys. Rev.*, (2), **20**. 113, 1922; R. L. Roman, *Brit. Pat. No.* 19543, 1893; 21186, 1895; H. Falkenberg, *ib.*, 247687, 1924; D. A. Roche, *Monit. Scient.*, (4), **7**. 269, 1893; E. C. Bain, *Met. Chem. Engg.*, **28**. 21, 1923; R. Wallace, *U.S. Pat. No.* 567757, 1896; A. St. John, *Tech. Publ. Amer. Inst. Min. Eng.*, 22, 1927; *Min. Met.*, **8**. 397, 1927; Hannoversche Industriegesellschaft, *German Pat., D.R.P.* 184476, 1905; H. Lieber, *ib.*, 251262, 1912; H. Falkenberg, *ib.*, 299052, 1914; H. Kuzel, *ib.*, 186980, 1906; H. Mennicke, *Die Metallurgie des Wolframs*, Berlin, 255, 1911; S. Inouye, *Mem. Coll. Kyoto*, **4**. 43, 1920; T. Goldschmidt, *French Pat. No.* 427774, 1911; J. G. Escard, *Génie Civil*, **55**. 74, 85, 1909; *Oesterr. Zeit. Berg. Hütt.*, **58**. 201, 215, 1910; E. Haynes, *Trans. Amer. Inst. Min. Eng.*, **44**. 573, 1913; *Journ. Ind. Eng. Chem.*, **5**. 189, 1913; *Eng. Min. Journ.*, **105**. 997, 1918; L. Freiherr, *Metall Erz*, **10**. 844, 1913; Z. Jeffries, *Trans. Amer. Inst. Min. Eng.*, **56**. 600, 1917; F. A. Fahrenwald, *ib.*, **56**. 612, 1917; A. E. van Arkel, *Physica*, **4**. 33, 1924; **6**. 64, 1926; P. Clausing, *ib.*, **7**. 193, 1927; H. von Miller, *Met.*, **9**. 63, 1912; R. B. Wheatley, *U.S. Pat. No.* 766085, 1904; *German Pat., D.R.P.* 131514, 1901; 187416, 1903; J. Webster, *ib.*, 29020, 1884; C. Berg, *ib.*, 90723, 1908; 123, 820, 1900; G. Roman, *ib.*, 82819, 1907; F. Jones, *U.S. Pat. No.* 998777, 1907.

§ 9. The Lower and Intermediate Oxides of Tungsten

About half a dozen tungsten oxides have been reported whose individuality is not well-established; and, in addition, there are the more clearly defined hemipentoxide, W_2O_5, the dioxide, WO_2, and the trioxide, WO_3. E. D. Desi [1] obtained a blue product by the action of conc. sulphuric acid on tungsten at 200°; after quickly washing with alcohol and ether, and rapid drying, its composition approximated *tungsten monoxide*, WO, or $W_2O.WO_2$; if boiling conc. sulphuric acid be employed, a mixture of a white and a greenish-blue product is formed—the latter, when separated, washed with alcohol and ether, and rapidly dried, corresponds in composition with *tungsten tetritatrioxide*, W_4O_3. If tungsten be heated with conc. sulphuric acid in a sealed tube at 150°, a blue product with the composition of *tungsten hemitrioxide*, W_2O_3, is formed; and if the temp. in the sealed tube be 180°, the blue product has the composition of *tungsten pentitaenneaoxide*, W_5O_9. When these oxides are treated with ammonia, or alkali-lye, tungsten and the trioxide are formed; and the hemitrioxide precipitates silver in brilliant scales from silver nitrate soln.

Another series of blue-coloured oxides has been reported intermediate between the di- and trioxides. They are formed either by oxidizing the dioxide or by reducing the trioxide. A. Lottermoser suggested that E. D. Desi's oxides, as well as these intermediate oxides, are only mixtures of tungsten and its trioxide. A number of these have been used as blue pigments under the commercial names *wolfram-blue, mineral blue*, and *blue carmine*. E. F. Anthon added that these blues are cheaper than the smalt blues. A. Pinchon employed a mixture of tungsten-blue and yellow tungstic acid as a non-poisonous green pigment in place of the arsenical copper greens. J. J. Berzelius observed that when dry hydrogen is passed over gently warmed tungsten trioxide, a blue oxide is formed—F. J. Malaguti used the flame of a spirit-lamp as a source of heat; and A. Riche recommended working at 250°. F. Göbel, and L. Gmelin obtained the blue oxide by passing carbon monoxide over tungsten trioxide at a red-heat. F. J. Malaguti, and L. von Uslar obtained the blue oxide by igniting ammonium tungstate in a covered crucible; and E. F. Anthon, by heating the ammonium tungstate in a current of hydrogen—*vide infra*, the 5 : 14, 4 : 11, and 3 : 8 oxides; and also the analogous blue molybdenum oxides.

There are some hydrated forms of the blue oxide—thus, A. Riche observed that when tungstic acid under water is exposed to sunlight, it acquires a blue colour; and R. E. Liesegang, that tungstic acid in contact with paper, becomes blue in sunlight. R. Bunsen said that paper moistened with sodium tungstate soln. becomes blue or green when treated with stannous chloride, or ammonium sulphide. H. E. Roscoe observed that when tungsten pentachloride or pentabromide is hydrolyzed, the blue oxide is formed, and this is easily oxidized by permanganate to tungstic acid. P. Burckhard obtained the blue product by the electrolysis of fused sodium tungstate; and E. F. Smith, by the electrolysis of fused sodium tungstate, and by the electrolysis of a soln. of a tungstate in boiling hydrochloric acid. C. Scheibler added that when a soln. of metatungstic acid is sat. with hydrogen sulphide, and then treated with ammonia or ammonium sulphide, sulphur separates out, and the mixture acquires an intense blue coloration. W. Biltz found that the blue colloidal soln. so prepared dyes silk a pale blue—the result is less satisfactory with cotton or wool. W. Biltz dialyzed the colloidal soln. and found that some of the blue substance passes through the membrane. The dialyzed soln. is deep sky-blue. M. Kröger obtained colloidal soln. of the blue tungsten oxide by electrolyzing a 2 per cent. soln. of sodium tungstate with an excess of acid; if an excess of acid be not used, a dark brown soln. is formed. The colloid is reversible, and the colloid is negative so that it collects about the anode as a dark blue liquid when an electric current is passed through the liquid contained in A. Coehn's apparatus. The liquid about the cathode becomes clear. The colloid is precipitated from the soln. by positively charged colloids—*e.g.* the hydrated oxides of iron, aluminium, chromium, thorium, zirconium, and cerium. W. Biltz and W. Geibel found that a freshly-prepared colloidal soln. of the blue oxide is optically empty, older preparations are more or less cloudy in Tyndall's cone of light. N. R. Dhar and co-workers studied the coagulation of the colloidal soln.

According to E. T. Allen and V. H. Gottschalk, *tungsten pentitatetradecoxide*, $W_5O_{14}.H_2O$, is formed when tungsten trioxide is reduced by heating it with soln. of stannous chloride in hydrochloric acid on a water-bath, or by heating it to 200° with hydriodic acid in a sealed tube. The *pentitatetradecoxide* forms a dark blue powder with a purplish lustre; it is insoluble in water acidified with hydrochloric acid, but in pure water it seems to form a colloidal soln. It is readily oxidized by exposure to the air or by oxidizing agents, and is instantly converted into the trioxide by the action of heat. When heated with a soln. of an alkali hydroxide, hydrogen is evolved and a tungstate is produced, whilst by the action of ammonia, ammonium tungstate and a brown residue are formed, but no gas is evolved. According to E. D. Desi, when sulphurous acid acts on tungsten, W_5O_{14} is formed. J. Eltzbacher found that when freshly precipitated tungsten trioxide is dissolved in a boiling soln. of oxalic acid, and the liquid electrolyzed in a compartment cell, the cathode liquid becomes clear, and a deposit of the dark blue oxide forms on the cathode. H. Leiser stated that if an acidic soln. of tungstic acid is electrolyzed, using a platinum or nickel cathode, a blue soln. of *tungsten tetritahenoxide*, W_4O_{11}, the anhydride of metatungstic acid, is formed. L. von Uslar reported *tungsten pentitaoctoxide*, W_5O_8. As indicated above, when the pentitatetradecoxide is treated with aq. ammonia, a brown mass is produced which E. T. Allen and V. H. Gottschalk found to have the composition of *tungsten tritaoctoxide*, $W_3O_8.H_2O$, when it has been washed and dried. The deep purple oxide has a bronze lustre, and its chemical behaviour is like that of the pentitatetradecoxide. E. D. Desi said that the tritaoctoxide, W_3O_8, is obtained by heating ammonium metatungstate to a bright red-heat, or by fusing tungstic acid with potassium iodide. The purple product has a yellow metallic lustre, and it is insoluble in acids, and alkali-lye. O. F. von der Pfordten also prepared this oxide.

L. Wöhler and O. Balz measured the equilibrium constants of the systems in which tungsten trioxide and dioxide are reduced by hydrogen; and in which tungsten is oxidized by steam. The equilibrium constant is represented by the ratio of the concentrations of steam, C_{H_2O}, and of hydrogen, C_{H_2}, in equilibrium with the solid phase. Only the bluish-violet **tungsten hemipentoxide,** W_2O_5, and brown tungsten dioxide, WO_2, were found as stable solid phases. The blue oxides with a composition between that of the trioxide and of the hemipentoxide are mixtures. These results were confirmed by G. Chaudron—*vide supra*, Fig. 2. L. Wöhler and O. Balz found that the equilibrium constants were $K_1=16$ for $WO_3 : W_2O_5$ at 800° ; $K_2=5{\cdot}1$ for $W_2O_5 : WO_2$ at 800° ; and $K_3=1{\cdot}0$ for $WO_2 : W$ at 950°. L. Wöhler and W. Prager gave :

	733°	828°	863°	868°	941°	1036°
K_3 . .	0·45	0·65	0·75	0·82	0·99	1·29

J. A. M. van Liempt showed that the conditions of equilibrium indicate that if hydrogen be passed through water at 95°, and the mixture of hydrogen and water vapour be passed over tungsten trioxide at 900°, tungsten hemipentoxide is formed. The blue oxide obtained by W. Reinders and A. W. Vervloet varied in composition between $WO_{2{\cdot}20}$ to $WO_{2{\cdot}95}$. G. A. Meerson found that in hydrogen, the hemipentoxide sublimes above 900°. L. Wöhler and R. Günther calculated for the dissociation press., p_2 atm., for $W_2O_5 \rightarrow WO_2$, $\log p_2=-28000T^{-1}+8{\cdot}496$; and for the heat of the reaction, 128·0 Cals. H. Alterthum and F. Koref calculated values for the dissociation press., and gave for the heat of vaporization 43·36 Cals. at 1800° K. For the equilibrium constant in the reaction $4WO_2+O_2=2W_2O_5+237$ Cals., $K_2=[WO_2]^4[O_2]/[W_2O_5]^2$, where the bracketed terms denote partial press., $\log K_2=-237000T^{-1}/4{\cdot}57+3\times1{\cdot}75\log T+9$. W. Fränkel found for the reaction $2WO_3+CO \rightleftharpoons CO_2+W_2O_5$, for $K=[CO_2]/[CO]$ between 750° and 1050°, $K=17{\cdot}2$ to 21·1—*vide infra*, tungsten trioxide. Z. Shibata gave $2WO_2+\frac{1}{2}O_2=W_2O_5+62{\cdot}9$ Cals. P. Sabatier and J. B. Senderens said that tungsten dioxide at 450°–500° is oxidized by nitrous or nitric oxide to tungsten hemipentoxide. The various intermediate oxides, prepared in the dry-way as indicated above, must be regarded as mixtures containing blue hemipentoxide. E. Friederich and L. Sittig obtained the dark violet hemipentoxide by heating at 1000° for an hour a mixture of 4·77 grms. of powdered tungsten and 29 grms. of tungsten trioxide. H. Leiser obtained a blue oxide approximating W_4O_{11} by the electrolysis of metatungstic acid with a platinum cathode, and with a lead cathode the dioxide is formed. J. A. M. van Liempt gave for the heat of formation $4WO_2+O_2=2W_2O_5+125{\cdot}2$ Cals. ; or $2(2W,5O)=318{\cdot}4$ Cals. E. Friederich gave 4·56 ohm. per sq. mm. for the electrical resistance. The blue oxide has been obtained only in an impure state as an amorphous powder ranging in colour from a greenish-blue to deep blue. The X-ray diffraction pattern obtained by C. J. Smithells and H. P. Rooksby is shown by Fig. 14. E. Friederich and L. Sittig gave $4{\cdot}5\times10^4$ ohms for the sp. resistance at 100°, and found it to be less than the resistance of the dioxide. E. Wedekind and C. Horst gave $0{\cdot}755\times10^{-6}$ for the magnetic susceptibility. The blue oxide is converted into the trioxide when heated in air or oxygen ; and when prepared in the wet way, it is readily oxidized by nitric acid or aqua regia, but when prepared in the dry way it resists attack by these reagents. V. I. Spitzin and L. Kaschtanoff observed that when the hemipentoxide is heated in hydrogen chloride, the dioxydichloride is formed, leaving a residue of tungsten ; and he represented the composition : $W(WO_3)_5$, *i.e.* $3W_2O_5$. P. Sabatier and A. Mailhe said that above 170°, the blue oxide acts catalytically in decomposing formic acid into carbon monoxide and water. The catalytic properties of the blue oxide in forming ethyl alcohol, etc., were studied by P. Sabatier and A. Mailhe, and J. N. Pearce and A. M. Alvarado. A. Charriou demonstrated the increased catalytic activity of alumina containing the adsorbed blue oxide.

J. J. Berzelius[2] obtained **tungsten dioxide,** WO_2, by passing hydrogen over tungsten trioxide, free from alkali, and feebly ignited in a glass tube. A. Riche added that if the temp. be too low, the blue oxide is formed, and if too high the metal is formed. In the formation of the dioxide as an intermediate stage in the reduction of tungsten trioxide by hydrogen, J. A. M. van Liempt showed that the conditions of equilibrium indicate that if hydrogen be passed through water at 85°, and the mixture of hydrogen and water vapour be passed over tungsten trioxide at 900°, tungsten dioxide is formed—*vide supra.* W. Fränkel made similar observations in connection with the reduction of carbon monoxide—*vide infra,* tungsten trioxide. C. F. Bucholz heated a mixture of tungsten trioxide and carbon in a covered crucible at a dull red-heat; the Westinghouse Metal Filament Lamp Co. added that better results are obtained with a mixture of tungsten trioxide, free from alkali, and one-tenth to one-fifth its weight of glycerol, or ethylene glycol. The dried mass is heated in a closed vessel at a bright red-heat for some hours. F. Wöhler allowed dil. hydrochloric acid and zinc to act on tungsten trioxide, if necessary renewing the acid, and zinc, until all trioxide had been converted into copper-red scales. The product is washed with water while protected from air, and preserved under water. O. F. von der Pfordten used hydrated tungsten trioxide. A. Riche added that the tungsten trioxide is only superficially reduced by this process, and he recommended the use of an alkali tungstate in place of tungsten trioxide, and washing the product with water saturated with hydrogen, and afterwards drying it in an atm. of hydrogen. F. Wöhler heated an intimate mixture of potassium tungstate and ammonium chloride until the ammonium salt was all expelled; washed out the potassium chloride with water, and the undecomposed acid tungstate with a boiling dil. soln. of potassium hydroxide; and finally washed the product with water. F. Wöhler, and H. E. Roscoe decomposed tungsten tetrachloride with water and obtained a precipitate of the dioxide and a greenish-brown soln. which gradually deposited the dioxide; tungsten dichloride is also hydrolyzed by water slowly giving off hydrogen and forming the dioxide. E. Defacqz heated tungsten diiodide to 500° in a current of carbon dioxide. E. D. Desi obtained the dioxide by evaporating sulphuric acid along with tungsten monoxide. L. A. Hallopeau heated lithium paratungstate for nearly an hour in a current of hydrogen, and washed the product successively with boiling water, conc. hydrochloric acid, a 20 per cent. boiling soln. of lithium hydroxide, and finally with hot water. E. Friederich and L. Sittig obtained the dioxide by heating a mol of the triiodide and a gram atom of carbon; and also by heating to 1000° for an hour, an intimate mixture of a gram-atom of tungsten powder and 2 mols of tungsten trioxide. H. Leiser observed that a soln. of a metatungstic acid when electrolyzed with a lead cathode furnishes tungsten dioxide, and with a platinum cathode, a blue oxide approximating W_4O_{11}. W. Meissner, and A. Schulze discussed the supraconductivity of the dioxide; and J. S. Donal, the emission of electrons by tungstous oxide. J. Vrede observed that the oxide is no use as a radio-detector.

R. F. Bernhardi-Grisson said the electrolytic reduction of soln. of tungsten trioxide in hydrofluoric or hydrochloric acid furnishes the *dihydrate,* $WO_2.2H_2O$, **tungsten tetrahydroxide,** H_4WO_4, or $W(OH)_4$. It is a brown powder soluble in hydrochloric acid forming a greenish soln. which rapidly becomes blue owing to the oxidation of quadrivalent to quinquevalent tungsten. It is insoluble in soda-lye, sulphuric acid, and acetic acid.

J. J. Berzelius described tungsten dioxide as a brown powder with a tinge of copper-red; and A. Riche found his preparation to be dark yellow. F. Wöhler said that it forms copper-red scales with a metallic lustre; and L. A. Hallopeau, a brown powder, with a copper-red lustre, consisting of microscopic, opaque, regular, octahedral crystals. V. M. Goldschmidt and co-workers discussed the crystal structure. L. Pauling discussed the crystal structure. C. J. B. Karsten gave 12·11 for the sp. gr. W. Biltz studied the mol. vol. E. Friederich and L. Sittig gave 5·0 to 5·5 for the hardness. L. Wöhler and R. Günther calculated for the dissociation press. p_3 atm., for $WO_2 \rightarrow W$, $\log p_3 = -29808T^{-1} + 9{\cdot}168$; and for the heat of the reaction: $W + O_2 = WO_2 + 136{\cdot}2$ Cals. N. Parravano and G. Malquori gave for the dissociation press., $\log p_{O_2} = -24{\cdot}993$ at 600°. H. Alterthum and F. Koref calculated values for the equilibrium constant in the equation $W + O_2 = WO_2 + 82{\cdot}6$ Cals., $K_1 = [WO_2]/[O_2]$, where the bracketed terms denote partial press., and log

$K_1=82600T^{-1}\div 4{\cdot}57$. They gave for the heat of vaporization, 48·86 Cals. at 2000° K. Z. Shibata gave 138·2 cals. per gram. E. Friederich and L. Sittig gave 1500°–1600° for the m.p. J. A. M. van Liempt gave for the heat of formation $(W,O_2)=127{\cdot}9$ Cals.; and for the heats of oxidation, $(4WO_2,O_2)=2W_2O_5+125{\cdot}2$ Cals.; and $(2W_2O_5,O_2)=4WO_3+140{\cdot}4$ Cals. The X-ray diffraction pattern, obtained by C. J. Smithells and H. P. Rooksby, is shown in Fig. 14. H. von Wartenberg and H. Moehl observed that the heat of formation of WO_2 is 131 Cals., and the heat of vaporization −31 cals. E. Friederich found the electrical resistance to be $9{\cdot}8\times10^4$ ohms at 1000°. When the dioxide is heated in **hydrogen,** F. Wöhler said that it is reduced to the metal—*vide supra,* the action of water-vapour on tungsten: $W+2H_2O\rightleftharpoons WO_2+2H_2$. The powder obtained by the hydrogen reduction process is pyrophoric, but, according to A. Riche, after it has stood 24 hrs. in hydrogen, it is stable in **air.** When the dioxide is heated in air, it burns like tinder to form the trioxide. The dioxide, freshly prepared by the wet-process, rapidly oxidizes in air, acquiring a blue colour; if the powder has been dried, it may be kept in contact with air without change. The dioxide burns to the trioxide when heated in **oxygen;** and the same product is obtained when the dioxide is heated with **mercuric oxide.** If **water** be in contact with the dioxide for some months, it acquires a blue colour. S. M. Délepine and L. A. Hallopeau found that the dioxide readily decomposes water containing a little alkali in consequence of the formation of an alkali tungstate. J. J. Berzelius said that a conc. boiling soln. of **potassium hydroxide** decomposes the dioxide forming the alkali tungstate, and giving off a little hydrogen; and A. Riche, and E. F. Smith and O. L. Shinn added that the soln. in alkali-lye becomes intensely red, it gives off hydrogen, and then acquires a blue colour. L. A. Hallopeau's preparation was not attacked by conc. alkali-lye. H. E. Roscoe observed that the dioxydichloride is formed when dry **chlorine** acts on the dioxide; and A. Riche, and E. F. Smith and O. L. Shinn added that chlorine-water oxidizes the dioxide to the trioxide. V. I. Spitzin and L. Kaschtanoff found **hydrogen chloride** converts it into the dioxydichloride and tungsten; and they wrote the formula $W(WO_3)_2$, *i.e.* $3WO_2$. L. A. Hallopeau found that the dioxide is attacked neither by **hydrochloric acid** nor by **sulphuric acid.** A. Riche, and E. F. Smith and O. L. Shinn added that a little of the dioxide prepared by the wet process dissolves in cold hydrochloric or sulphuric acid forming a reddish soln. which becomes purple when heated; the soln. remains red for a long time, but it slowly decomposes forming the blue oxide. The change occurs rapidly if the soln. is heated. E. F. Smith and H. Fleck found that **sulphur monochloride** converts the dioxide into the oxytetrachloride. According to F. Wöhler, when gently warmed in dry **ammonia,** the dioxide forms a brownish-black substance containing hydrogen and nitrogen, mixed with unchanged dioxide, and at a higher temp., tungsten is formed. A. Riche, and E. F. Smith and O. L. Shinn found that boiling, aq. ammonia does not dissolve the dioxide. According to P. Sabatier and J. B. Senderens, if the dioxide is heated to 450° or 500° in **nitrous oxide,** the blue hemipentoxide is formed—neither nitric oxide nor nitrous fumes were observed, the nitrous oxide is reduced to nitrogen. At about 500°, tungsten dioxide reacts vigorously with **nitric oxide** forming the blue hemipentoxide; and at about 300°, **nitrogen peroxide** forms a mixture of tungsten hemipentoxide and trioxide. A. Riche, E. F. Smith and O. L. Shinn, and L. A. Hallopeau observed that cold **nitric acid** slowly oxidizes the dioxide to the trioxide; and A. Riche found that **aqua regia** forms a similar product. H. C. Greenwood found that the dioxide is reduced to the metal when it is heated with **carbon** to about 1020°. O. Brunner showed that when tungsten dioxide is heated with **carbon dioxide** it is oxidized: $WO_2+CO_2=WO_3+CO$. A. Riche, and E. F. Smith and O. L. Shinn found that the dioxide reduces an ammoniacal soln. of **silver nitrate** to silver; and **cupric and mercuric chlorides** are reduced to cuprous and mercurous chlorides respectively. H. von Wartenberg and H. Moehl found that there is a balanced reaction at high temp. With **aluminium, zirconium,** and **thorium** and tungsten dioxide, *vide* *supra*, the chemical properties of tungsten. F. Wöhler found that when a mixture of the dioxide and **sodium carbonate** is heated out of contact with air, tungsten and sodium tungstate are formed.

F. Wöhler[3] observed that when acid sodium tungstate is reduced by hydrogen, a bronze-coloured powder is obtained. The product is a member of a series of reduction products of the alkali and alkaline earth tungstates which have been designated **tungsten-bronzes** because, owing to their intense and vivid colours, and their remarkable chemical inactivity, they can be used as substitutes for *bronze-powders.* This term is applied to finely-divided or powdered metals—*e.g.* brass, bronze, aluminium, and copper—which, when mixed with a suitable binding material—*e.g.* varnish, or amyl acetate—can be used as paints for ornamental and decorative purposes, and for protecting iron, etc., against corrosion.

The tungsten-bronzes appear to contain several sexivalent tungsten atoms, and one quadrivalent tungsten atom. Their composition can be represented by $mR_2O.nWO_3.WO_2$, although in the majority of them m is unity, and the general formula is then $R_2O.nWO_3.WO_2$, or simply $R_2(WO_3)_{n+1}$. The chemical nature of the tungsten-bronzes has not been worked out. Many of them are probably solid soln. of different individuals. Different formulæ have been applied to the products of apparently similar reactions. Thus, G. von Knorre heated equimolar proportions of sodium and potassium tungstates to redness in hydrogen and obtained on one occasion a purple-red bronze, $2Na_4W_5O_{15}.5K_2W_4O_{12}$, and on another occasion a dark red bronze, $2Na_2W_3O_9.3K_2W_4O_{12}$. Different products have probably been given the same formula. Each new investigation furnishes new products, but rarely are the reports of previous workers completely confirmed. There are difficulties (i) in the analytical determination of the ratio of the total tungsten to that present in the quadrivalent form (ii) in recognizing whether the products are chemical individuals or mixtures because of their general insolubility, and resistance to attack by ordinary reagents. When heated in hydrogen chloride, V. I. Spitzin and L. Kaschtanoff found that the dioxydichloride is formed, sodium chloride, and tungsten are formed, and they think that their results agree with the formula $(Na_2W_2O_6)_3$, or $Na_6[(WO_4)_3W(WO_3)_2]$, for the yellow bronzes; and $(Na_2W_3O_9)_3$, or $Na_6[(WO_4)_3(WO_3)_3W(WO_3)_2]$, for the red bronzes. (iii) In repeating the work of previous investigators because of unrecognized but essential conditions for producing particular results. In some cases, arrested reactions are involved—*vide* **4**. 31, 33. Thus, O. Brunner showed that the reaction with the yellow sodium tungsten bronze: $3Na_2W_2O_6 \rightleftharpoons Na_2WO_4+2Na_2W_2O_7+W$, is reversible, and if it be slow, or if the temp. be variable, it will be difficult to obtain a definite product.

The tungsten-bronzes are obtained: (1) by the reduction of an acid tungstate with hydrogen, coal gas, or tin, zinc, or iron at a high temp.—F. Wöhler, and H. Wright; (2) by the electrolytic reduction of a fused polytungstate—C. Scheibler, A. Stavenhagen, E. Engels, L. and H. H. Kahlenberg, and E. Zettnow; and (3) by melting mixtures of normal or acid tungstates with tungsten dioxide, out of contact with air—O. Brunner. According to V. I. Spitzin, the tungstates are reduced by hydrogen at 650° to 700° to a constant weight; and the products from the ditungstate, $Na_2W_2O_7$, paratungstate, $Na_{10}W_{12}O_{41}$, tetratungstate, $Na_2W_4O_{13}$, and pentatungstate, $Na_2W_5O_{16}$, are, in every case, mixtures of sodium tungstate, Na_2WO_4, and tungsten. Above 700°, a further loss in weight takes place, and at 900°, each of the above acid tungstates and also sodium tungstate are reduced to tungsten. The various tungsten bronzes are also reduced to sodium tungstate and tungsten at 650°–700°. The blue bronze, $Na_2W_5O_{15}$, is reduced successively to the violet, $Na_2W_4O_{12}$, the red, $Na_2W_3O_9$, and the yellow bronzes, $Na_2W_2O_6$; this reduction takes place comparatively slowly at 550° and rapidly at 650°, but at no temperature does reduction cease at any intermediate stage. The formation of bronzes by the reduction of acid tungstates is believed to take place according to equations of the type: $Na_2W_4O_{13}+H_2=Na_2W_4O_{12}+H_2O$; $Na_2W_4O_{12}+3H_2=Na_2W_3O_9+W+3H_2O$. In this case, the molecule of bronze could never contain more atoms of tungsten than that of the tungstate from which it was prepared. This, however, is sometimes the case, but is ascribed to impurities in the tungstate; thus, sodium tetratungstate yields a blue bronze, but the metatungstate, $Na_2W_4O_{13},10H_2O$, which can be purified by crystallization from water, yields the violet bronze.

The colour of the tungsten bronzes ranges from golden-yellow, reddish-yellow, purple-red, violet, blue, to bluish-black. As the proportion of tungsten increases, the colour changes in the order indicated. In thin layers, the bronzes are more or less translucent, and the colour by transmitted light may be complementary to that by reflected light. These bronzes are usually crystalline—generally as cubes or needles. Their sp. gr. is high ranging from 6·5 to 7·5. For the luminescence of the tungsten-bronzes, *vide infra*, calcium tungstate. They are good conductors of electricity. They are insoluble in water; and with the exception of hydrofluoric acid are not attacked by the usual acids. Hot aqua regia acts on some of the tungsten bronzes. They are not acted on by alkali-lye, but they are decomposed by fusion with alkali hydroxide, sulphur, and ammonium hydrosulphate or persulphate. Some of the bronzes were shown by O. Brunner to be oxidized when heated with carbon dioxide to form carbon monoxide. They are oxidized to tungstates when heated in air or oxygen, or when heated with mercuric oxide. When boiled with an ammoniacal soln. of silver nitrate, silver is precipitated. O. Brunner showed that the tungsten-bronzes with a relatively small proportion of tungsten decompose when heated, forming tungsten, normal tungstate, and a tungsten-bronze with a higher proportion of tungsten, *e.g.* $3Na_2W_2O_6 \rightleftharpoons W + Na_2WO_4 + 2(Na_2WO_4.WO_3)$.

Lithium-tungsten-bronzes were prepared by O. Brunner, W. Feit, L. A. Hallopeau, G. von Knorre, and C. Scheibler. Thus, $Li_2W_4O_{12}$ furnishes steel-blue, microscopic plates of sp. gr. 7·50; $Li_2W_5O_{15}$ appears in deep blue, microscopic prisms when lithium paratungstate is fused with tin, or fused paratungstate is electrolyzed; $Li_2W_7O_{21}$ is steel-blue; and $Li_2W_5O_{15}.3K_2W_4O_{12}$ appears in violet needles when a fused mixture of equimolar proportions of lithium and potassium tungstates is reduced with tin.

Sodium-tungsten-bronzes were prepared by E. F. Anthon, O. Brunner, L. and H. H. Kahlenberg, F. J. Malaguti, F. Margueritte, H. Schnitzler, J. Philipp, J. Philipp and P. H. Schwebel, C. Scheibler, F. Wöhler, and H. Wright. Thus, $Na_2W_2O_6$ furnishes golden-yellow cubes of sp. gr. 7·28; $Na_2W_3O_9$, purple-red octahedra of sp. gr. 7·22; $Na_2W_4O_{12}$, violet needles of sp. gr. 7·195; and $Na_2W_5O_{15}$, blue cubes with a copper-red lustre. W. Feit, and G. von Knorre prepared $3K_2W_4O_{12}.2Na_2W_3O_9$, and $5K_2W_4O_{12}.2Na_2W_5O_{15}$ as indicated above. Both are dark red; the latter has a sp. gr. 7·117, and when powdered, becomes blue.

Potassium-tungsten-bronzes were prepared by O. Brunner, L. A. Hallopeau, G. von Knorre, A. Laurent, E. Schaefer, and E. Zettnow. The $K_2W_4O_{12}$ bronze furnishes reddish-violet prisms of sp. gr. 7·1. A suspension appears blue by transmitted and green by reflected light. G. von Knorre and E. Schaefer were of the opinion that this is the only potassium-tungsten-bronze known, but others have been reported—*e.g.* O. Brunner obtained reddish-violet $K_2W_3O_9$; a blue mixture $K_2W_4O_{12}+K_2W_5O_{15}$; and blue mixtures of the ultimate composition $K_2W_5O_{15}$, $K_2W_6O_{18}$, and $K_2W_8O_{24}$.

Alkali-alkaline earth-tungsten-bronzes were prepared by E. Engels by the electrolysis of fused mixtures of potassium or sodium tungstate with the calculated amount of alkaline earth carbonate. He reported the following products: $CaW_4O_{12}.5Na_2W_5O_{15}$, in blue pyramids; $CaW_4O_{12}.10Na_2W_3O_9$, in purple-red cubes or pyramids; $CaW_4O_{12}.5K_2W_4O_{12}$, in glistening red needles; $SrW_4O_{12}.5Na_2W_5O_{15}$, in violet pyramids; $SrW_4O_{12}.12Na_2W_5O_{15}$, in carmine-red pyramids; $SrW_4O_{12}.5K_2W_4O_{12}$, in red needles: $2BaW_4O_{12}.3Na_2W_5O_{15}$, in dark blue crystals; $BaW_4O_{12}.5Na_2W_3O_9$, in yellowish-red cubes; and $Ba_4O_{12}.5K_2W_4O_{12}$, in violet-red prisms.

Thorium-tungsten-bronzes.—C. J. Smithells inferred that the coloured thoria residues from dissolved thoriated tungsten filaments, which have been heated to a high temp., contain thorium-tungsten-bronzes.

References.

[1] N. R. Dhar, D. N. and M. N. Chakravarti, *Koll. Zeit.*, **44**. 225, 1928; E. D. Desi, *Journ. Amer. Chem. Soc.*, **19**. 213, 1897; A. Riche, *Ann. Chim. Phys.*, (3), **50**. 33, 1857; J. J. Berzelius, *Afhand. Fys. Kemi. Min.*, **4**. 293, 1815; *Schweigger's Journ.*, **16**. 476, 1816; L. von Uslar, *Zachr. Gött.*, **94**. 255, 1855; *Beiträge zur Kenntniss des Wolframs und Molybdäns*, Göttingen, 1855; C. Scheibler, *Chem. News*, **6**. 181, 1862; *Journ. prakt. Chem.*, (1), **83**. 313, 1861; E. F. Anthon, *ib.*, (1), **9**. 8, 1836; F. Göbel, *ib.*, (1), **6**. 386, 1835; *Bull. Soc. Nat. Moscou*, **9**. 312, 1836; H. E. Roscoe, *Liebig's Ann.*, **162**. 359, 1872; *Proc. Manchester Lit. Phil. Soc.*, **11**. 79, 1872; *Chem. News*, **25**. 61, 73, 90, 1873; *Bull. Soc. Chim.*, (2), **25**. 61, 1873; Z. Shibata, *Tech. Rep. Tohoku*, **8**. 129, 145, 1929; G. A. Meerson, *Journ. Russ. Phys. Chem. Soc.*, **60**. 12, 1928; J. N. Pearce and A. M. Alvarado, *Journ. Phys. Chem.*, **29**. 256, 1925; E. T. Allen and V. H. Gottschalk, *Amer. Chem. Journ.*, **27**. 328, 1902; F. J. Malaguti, *Ann. Chim. Phys.*, (2), **60**. 273, 1835; A. Charriou, *Journ. Chim. Phys.*, **23**. 673, 1926; H. Leiser, *Zeit. Elektrochem.*, **13**. 690, 1907; A. Coehn, *ib.*, **15**. 653, 1909; L. Wöhler and O. Balz, *ib.*, **27**. 406, 1921; L. Wöhler and W. Prager, *ib.*, **23**. 199, 1917; L. Wöhler and R. Günther, *ib.*, **29**. 276, 1923; H. Alterthum and F. Koref, *ib.*, **31**. 508, 1925; R. E. Liesegang, *Phot. Arch.*, **34**. 152, 1865; R. Bunsen, *Liebig's Ann.*, **138**. 257, 1866; O. F. von der Pfordten, *ib.*, **222**. 137, 1884; *Ber.*, **16**. 508, 1883; *Bull. Soc. Chim.*, (2), **40**. 368, 1883; L. Weiss, *Zeit. anorg. Chem.*, **65**. 327, 1910; J. A. M. van Liempt, *ib.*, **126**. 226, 1923; V. I. Spitzin and L. Kaschtanoff, *ib.*, **157**. 141, 1926; P. Sabatier and A. Mailhe, *Ann. Chim. Phys.*, (8), **20**. 289, 1910; *Compt. Rend.*, **152**. 1212, 1911; P. Sabatier and J. B. Senderens, *Bull. Soc. Chim.*, (3), **13**. 870, 1895; *Ann. Chim. Phys.*, (7), **7**. 348, 1896; *Compt. Rend.*, **120**. 618, 1895; G. Chaudron, *ib.*, **170**. 1056, 1920; *Études des réactions réversibles de l'hydrogène et de l'oxyde de carbone sur les oxydes métalliques*, Paris, 1921; W. Biltz, *Ber.*, **37**. 1095, 1771, 1904; *Nachr. Gött.*, 1, 1904; W. Biltz and W. Geibel, *ib.*, 141, 1906; E. Friederich, *Zeit. Physik*, **31**. 813, 1925; L. Gmelin, *Handbook of Chemistry*, London, **4**. 26, 1850; A. Lottermoser, *Jahresber.*, 892, 1897; A. Pinchon, *Polyt. Centr.*, 218, 1870; P. Burckhard, *Zeit. Chem.*, (2), **5**. 393, 1870; *Bull. Soc. Chim.*, (2), **14**. 35, 1870; E. F. Smith, *Ber.*, **13**. 753, 1880; E. Wedekind and C. Horst, *ib.*, **48**. 105, 1915; J. Eltzbacher, *Beiträge zur Elektrochemie der Wolframate*, 38, 1899; E. Friederich and L. Sittig, *Zeit. anorg. Chem.*, **145**. 127, 1925; M. Kröger, *Koll. Zeit.*, **30**. 16, 18, 1922; C. J. Smithells and H. P. Rooksby, *Journ. Chem. Soc.*, 1882, 1927; W. Fränkel, *Festschrift Jahrhundertfeier Inst. Frankfurt a. M.*, 136, 1924; W. Reinders and A. W. Vervloet, *Rec. Trav. Chim. Pays-Bas*, **42**. 625, 1923.

[2] J. J. Berzelius, *Afhand. Fys. Kemi Min.*, **4**. 293, 1815; *Schweigger's Journ.*, **16**. 476, 1816; C. F. Bucholz, *Schweigger's Journ.*, **3**. 1, 1811; A. Riche, *Ann. Chim. Phys.*, (3), **50**. 33, 1857; H. E. Roscoe, *Liebig's Ann.*, **162**. 359, 1872; *Proc. Manchester Lit. Phil. Soc.*, **11**. 79, 1872; *Chem. News*, **25**. 61, 73, 90, 1873; *Bull. Soc. Chim.*, (2), **25**. 61, 1873; C. J. B. Karsten, *Schweigger's Journ.*, **65**. 394, 1832; F. Wöhler, *Pogg. Ann.*, **2**. 345, 1824; *Quart. Journ. Science*, **20**. 177, 1826; *Phil. Mag.*, **66**. 263, 1825; *Ann. Chim. Phys.*, (2), **29**. 43, 1823; (3), **29**. 187, 1850; *Nachr. Gött.*, 35, 1850; *Liebig's Ann.*, **73**. 190, 1850; E. D. Desi, *Journ. Amer. Chem. Soc.*, **19**. 213, 1897; E. F. Smith and O. L. Shinn, *ib.*, **16**. 569, 1894; *Zeit. anorg. Chem.*, **7**. 47, 1894; E. F. Smith and H. Fleck, *ib.*, **21**. 1008, 1899; E. Friederich and L. Sittig, *ib.*, **145**. 127, 1925; P. Sabatier and J. B. Senderens, *Bull. Soc. Chim.*, (3), **13**. 870, 1895; *Ann. Chim. Phys.*, (7), **7**. 348, 1896; *Compt. Rend.*, **114**. 1429, 1892; **115**. 236, 1892; **120**. 618, 1895; S. M. Delépine and L. A. Hallopeau, *ib.*, **129**. 600, 1899; L. A. Hallopeau, *Ann. Chim. Phys.*, (7). **19**. 112, 1900; *Bull. Soc. Chim.*, (3), **19**. 748, 1898; (3), **21**. 266, 1899; *Compt. Rend.*, **127**. 512, 1898; E. Defacqz, *ib.*, **126**. 962, 1898; Westinghouse Metal Filament Lamp Co., *Brit. Pat. No.* 18922, 1907; O. F. von der Pfordten, *Bull. Soc. Chim.*, (2), **40**. 368, 1883; *Ber.*, **16**. 508, 1883; *Liebig's Ann.*, **222**. 158, 1884; H. von Wartenberg and H. Moehl, *Zeit. phys. Chem.*, **128**. 439, 1927; H. C. Greenwood, *Journ. Chem. Soc.*, **93**. 1493, 1908; C. J. Smithells and H. P. Rooksby, *ib.*, 1882, 1927; L. Pauling, *Journ. Amer. Chem. Soc.*, **49**. 765, 1927; J. A. M. van Liempt, *Zeit. anorg. Chem.*, **126**. 186, 226, 1923; V. I. Spitzin and L. Kaschtanoff, *ib.*, **157**. 141, 1926; R. F. Bernhardi-Grisson, *Die kathodische Reduktion der Wolframsäure*, Berlin, 1910; A. Rosenheim and R. F. Bernhardi-Grisson, *Ber. Internat. Cong. Appl. Chem.*, **7**. x, 120, 1911; O. Brunner, *Beiträge zur Kenntnis der Wolframbronzen*, Zürich, 1903; W. Reinders and A. W. Vervloet, *Rec. Trav. Chim. Pays-Bas*, **42**. 625, 1923; Z. Shibata, *Tech. Rep. Tohoku Univ.*, **8**. 129, 145, 1929; L. Wöhler and R. Günther, *Zeit. Elektrochem.*, **29**. 276, 1923; H. Alterthum and F. Koref, *ib.*, **31**. 508, 1925; H. Leiser, *ib.*, **13**. 690, 1907; E. Friederich, *Zeit. Physik*, **31**. 813, 1925; V. M. Goldschmidt, T. Barth, D. Holmsen, G. Lunde and W. Zachariasen, *Skrift. Nordske Akad.*, 1, 1926; W. Fränkel, *Festschrift Jahrhundertfeier Inst. Frankfurt a. M.*, 136, 1924; N. Parravano and G. Malquori, *Gazz. Chim. Ital.*, **58**. 279, 1928; A. Schulze, *Zeit. Metallkunde*, **22**. 311, 1930; W. Biltz, *Zeit. anorg. Chem.*, **193**. 321, 1930; K. Donal, *Phys. Rev.*, (2), **36**. 1172, 1930; W. Meissner, *Zeit. Ges. Kälte Ind.*, **37**. 174, 1930; J. Vrede, *Phys. Zeit.*, **31**. 323, 1930.

[3] F. Wöhler, *Pogg. Ann.*, **2**. 345, 1824; *Quart. Journ. Science*, **20**. 177, 1926; *Phil. Mag.*,

66. 263, 1825; *Ann. Chim. Phys.*, (2), **29.** 43, 1823; F. J. Malaguti, *ib.*, (2), **60.** 271, 1835; F. Margueritte, *ib.*, (3), **17.** 475, 1846; A. Laurent, *ib.*, (2), **67.** 219, 1838; H. Wright, *Liebig's Ann.*, **79.** 221, 1851; *Nachr. Gött.*, 181, 1851; C. Scheibler, *Chem. News*, **6.** 181, 1862; *Journ. prakt. Chem.*, (1), **80.** 204, 1860; (1), **83.** 273, 1861; E. F. Anthon, *ib.*, (1), **9.** 8, 1836; G. von Knorre, *ib.*, (2), **27.** 49, 1883; G. von Knorre and E. Schaefer, *Ber.*, **35.** 3407, 1902; E. Schaefer, *Beiträge zur Kenntnis der Wolframverbindungen*, Berlin, 1903; *Zeit. anorg. Chem.*, **38.** 142, 1904; V. I. Spitzin, *Journ. Russ. Phys. Chem. Soc.*, **58.** 474, 1926; *Zeit. anorg. Chem.*, **148.** 69, 1925; V. I. Spitzin and L. Kaschtanoff, *ib.*, **157.** 141, 1926; J. Philipp and P. H. Schwebel, *Ber.*, **12.** 2234, 1879; J. Philipp, *Monit. Scient.*, (3), **20.** 74, 1878; *Ber.*, **15.** 499, 1882; A. Stavenhagen, *ib.*, **32.** 3064, 1899; W. Feit, *ib.*, **21.** 133, 1888; E. Engels, *Zeit. anorg. Chem.*, **37.** 125, 1903; *Ueber Wolframbronzen*, Berlin, 1903; L. A. Hallopeau, *Bull. Soc. Chim.*, (3), **21.** 267, 1899; *Compt. Rend.* **127.** 512, 1898; C. J. Smithells, *Journ. Chem. Soc.*, **121.** 2236, 1922; L. and H. H. Kahlenberg, *Trans. Amer. Electrochem. Soc.*, **46.** 181, 1924; O. Brunner, *Beiträge zur Kenntnis der Wolframbronzen*, Zürich, 1903; E. Zettnow, *Pogg. Ann.*, **130.** 16, 241, 1867; H. Schnitzler, *Dingler's Journ.*, **211.** 484, 1874.

§ 10. Tungsten Trioxide

B. Silliman[1] observed the occurrence of a bright yellow, or yellowish-green, pulverulent earthy mineral which he called *tungstic ochre* at Monroe, Connecticut; it was called *oxide of tungsten* by W. Phillips; *acide tungstique*, by F. S. Beudant; *Wolframocker*, by C. C. von Leonhard; Wolframsäure, by F. von Kobell; Scheelsäure, and *Scheelocher*, by E. F. Glocker; *wolframine*, by R. P. Greg and W. G. Lettsom; and **tungstite,** by J. D. Dana. Its composition approximates **tungsten trioxide,** WO_3. R. P. Greg and W. G. Lettsom, and J. H. Collins found tungsten ochre in Callington and Gwennap, Cornwall; and in Carrock Fells, Cumberland. J. H. Collins called the ochre wolframite, and wolframite he called wolfram. F. S. Beudant referred to an occurrence as a yellow deposit on wolframite at Zinnwald, Bohemia, but J. J. Berzelius found no tungsten in the deposit, and V. R. von Zepharovich does not mention it. A. Lacroix observed its occurrence at La Vilate, Haupte-Vienne; and Vaubry, Pury-les-Vignes; and at Meymac, Corrèze; while P. A. Dufrénoy found it near Limoges. In addition to the occurrence at Monroe, Connecticut, J. D. Dana obtained the ochre from Cabarrus, Carolina; and F. D. Smith, from Osceola, Nevada. W. F. Petterd observed its occurrence at Ben Lomond, Tasmania. J. B. Scrivenor and J. C. Shenton observed a honey-yellow, crystalline mineral in the Kramat Pulai mine in the Federated Malay States. The crystals were rhombic; the sp. gr. 5·55; and the composition approximated $(ThO_2,Ce_2O_3,ZrO_2)H_2O+2WO_3.H_2O$, and the mineral was called **thorotungstite.**

The extraction of tungsten trioxide or tungstates from wolframite, scheelite, hübnerite, etc., has been previously discussed; so also has the purification of the tungsten trioxide. The trioxide is formed by the oxidation of the metal; I. Langmuir[2] observed that tungsten wires heated in oxygen at a low press. form the trioxide at about 530°, and above this temp. the oxide volatilizes. The trioxide is also obtained by roasting the lower oxides, or the oxynitrogen compounds, the hydrated tungsten oxides, ammonium tungstate, ammonium oxyfluotungstates, or tungsten sulphide. As previously indicated, hydrated tungsten trioxide is precipitated by adding an acid to a soln. of a tungstate. J. A. M. van Liempt studied the influence of temp. and the conc. of the acid on precipitated tungsten trioxide. The precipitate consists of a mixture of the white and the yellow forms of the trioxide, together with an adsorption compound with water. Temp. has little effect on the precipitation, but in order to obtain the precipitate in a granular and easily manipulated form, it is advisable to use an excess of highly conc. hydrochloric or nitric acid. The rate of precipitation depends on the method of mixing the soln. When the sodium tungstate soln. is added drop by drop to the acid, the rate of precipitation depends on the degree of ionization of the acid. Thus, 0·25*N*-nitric, perchloric, and hydrochloric acids showed very nearly identical precipitation curves, whilst 0·25*N*-sulphuric acid showed a much more extended period of induction, before precipitation started. This last curve, however, was very similar to that given by 0·18N-hydrochloric acid, the dissociation of which is about equal to that of 0·25N-sulphuric acid. When the acid was added to the tungstate soln., the slower the addition of the acid (up to the limit of twelve minutes) the slower was the subsequent precipitation of the tungstic acid. Y. Nakazawa and T. Okada prepared tungstic acid (i) by evaporating a soln. of the trioxide in conc. hydrochloric acid and obtained crystals of $WO_3.H_2O$; (ii) by passing steam into the soln. of the trioxide in conc. hydrochloric acid and obtained crystals of $WO_3.H_2O$; and (iii) by diluting the conc. hydrochloric acid at ordinary temp. and obtained a white acid, $WO_3.7H_2O$, difficult to filter. According to F. A. Bernoulli, and A. Safarik, the lemon-yellow, amorphous tungsten trioxide obtained by these methods can be converted into the crystalline form by strongly heating the product; according to A. E. Nordenskjöld, by fusing the hydrated trioxide with borax and washing the cold mass with hydrochloric acid, and aq. ammonia ; and, according to H. Debray, by passing a current of hydrogen chloride over the trioxide, or over a red-hot mixture of sodium tungstate and carbonate. E. Zettnow, and J. Waddell noticed the formation of some crystals when the trioxide is heated in hydrogen. A. Pinagel found a sample of commercial tungsten trioxide with 1·35 per cent. silica, 0·13 per cent. molybdenum trioxide, and traces of vanadium, iron, manganese, and sodium.

For α- and β-forms of tungsten trioxide, *vide supra*, the oxidation of tungsten. The **crystals** obtained by A. E. Nordenskjöld were small, bright yellow, transparent, rhombic prisms with the axial ratios $a:b:c=0·7002:1:0·3991$, or 0·6966 : 1 : 0·4026 ; and those obtained by H. Debray were octahedral—some were yellow and translucent, others dark green and opaque. P. Niggli studied the electronic structure. The crystals are sometimes thin, dark blue or green needles. H. C. Burger added that the X-radiograms of both the yellow and green forms are the same. H. E. Roscoe attributed the discoloration to the presence of small traces of sodium salts ; this was confirmed by N. H. Smith and H. S. Lukens. J. A. M. van Liempt attributed it to the reducing action of the dust particles in the air, a reaction which is favoured by exposure to light. L. Gmelin attributed the green coloration to the presence of reducing gases during the ignition of the oxide. N. H. Smith and H. S. Lukens showed that these hypotheses are not likely because, as shown by J. B. A. Dumas, and F. A. Bernoulli, the green oxide cannot be converted into the yellow oxide by ignition in a current of oxygen or nitrous oxides. J. J. and F. de Elhuyar gave 6·13 for the **specific gravity** of the amorphous, yellow oxide ; W. Herapath gave 5·274 at 16·5° ; A. E. Nordenskjöld, 6·302 to 6·384 ; and C. J. B. Karsten, 7·1306 ; while E. Zettnow gave 7·16 at 17° for the amorphous oxide, and 7·232 at 17° for the crystals. E. F. Smith and F. F. Exner gave 7·157 for the sp. gr. of the trioxide obtained by heating the hydrate to bright redness. H. P. Walmsley gave 7·146 for the sp. gr. of the dispersed oxide. The sp. gr. of tungsten ochre is 6·3 to 7·2.

The mol. vols. were studied by H. Schröder, C. del Fresno, W. Biltz, and D. Balareff. O. Ruff and A. Riebeth discussed the **plasticity** of mixtures of the oxide with water, etc. H. V. Regnault gave 0·0798 for the **specific heat,** and H. Kopp, 0·0894. According to A. S. Russell, the sp. ht. between −189° and −80·9° is 0·0442 ; between −75·8° and 0°, 0·0678 ; and between 2·3° and 46·6°, 0·0783 ; the corresponding **molecular heats** are 10·25, 15·73, and 18·16. F. M. Jäger and E. Rosenbohm gave $c_p=0·0503755+0·13644\times10^{-3}\theta-0·0490476\times10^{-6}\theta^2$ for the sp. ht. up to 1300° of the crystalline, yellowish-green oxide formed by heating tungsten to 1300°. J. Maydal discussed the sp. ht. When heated, the colour of tungsten trioxide deepens to a dark orange, but on cooling, the lemon-yellow colour is restored. E. D. Clark found that the yellow oxide is decomposed in the oxy-hydrogen flame—presumably by hot reducing gases. A. Riche said that the trioxide can be fused in the gas blowpipe flame, and the mass, on cooling, furnishes tabular crystals. W. D. Bancroft and H. B. Weiser found that when tungsten trioxide is introduced into the oxyhydrogen flame, the flame deposits a bright, lustrous, metallic mirror on a cold surface. F. M. Jäger and H. C. Germs gave 1473° for the **melting point ;** but C. Matignon said that it does not melt at 2130°. A. A. Read observed no change in the composition of the oxide after it had been heated to 1750°. W. R. Mott studied the volatilization of the oxide in the electric arc ; and I. Langmuir found that in an atm. of oxygen under reduced press., the trioxide formed on the surface of wire volatilizes above 530°, and the heated wire at about 930°. H. Copaux found that at a moderate red-heat tungsten trioxide is stable, but volatilization occurs at a bright red-heat so much so that 500 mgrms. lost 3 mgrms. in 5 min. G. A. Meerson also found that the trioxide volatilizes in moist hydrogen above 850°. L. Wöhler and R. Günther calculated for the **dissociation pressure,** p_1 atm., for the reaction $WO_3 \rightarrow W_2O_3$, log $p_1 = -28750T^{-1} + 10{\cdot}53$, and for the heat of the reaction, 131·4 Cals. If p_2 likewise denotes the dissociation press. of $W_2O_5 \rightarrow WO_2$ (*q.v.*), and p_3, that of $WO_2 \rightarrow W$ (*q.v.*), then,

T° K. .	873°	1073°	1273°	1473°	1673°	2800°	3200°	3300°
p_1 .	$10^{-24{\cdot}4}$	$10^{-18{\cdot}3}$	$10^{-14{\cdot}2}$	$10^{-11{\cdot}1}$	$10^{-8{\cdot}7}$	1·0	—	—
p_2 .	$10^{-25{\cdot}6}$	$10^{-19{\cdot}7}$	$10^{-15{\cdot}6}$	$10^{-12{\cdot}6}$	$10^{-10{\cdot}3}$	—	—	1·0
p_3 .	$10^{-26{\cdot}9}$	$10^{-20{\cdot}7}$	$10^{-16{\cdot}4}$	$10^{-13{\cdot}2}$	$10^{-10{\cdot}7}$	—	1·0	—

F. Born discussed this subject. H. Alterthum and F. Koref also calculated values for the dissociation press. ; and they found the **heat of vaporization** to be 40·64 Cals. at 1700° K. For the equilibrium condition in the reaction $2W_2O_5 + O_2 = 4WO_3 + 56{\cdot}7$ Cals., $K_3 = [W_2O_5]^2[O_2]/[WO_3]^2$ when the bracketed symbols denote partial press., log $K_3 = -56700T^{-1}/4{\cdot}57 - 1{\cdot}75 \log T^{-3}$. S. M. Delépine and L. A. Hallopeau gave for the **heat of formation** (W,3O)=195·41 Cals. at constant vol., and 196·3 Cals. at constant press. ; J. E. Moose and S. W. Parr, 194·9 Cals. ; Z. Shibata, 199·9 Cals. ; W. G. Mixter, 196·3 Cals. ; and L. Weiss, 192·648 to 196·146 at constant vol. S. M. Delépine and L. A. Hallopeau gave (WO_2,O)=64·63 Cals. at constant vol., and 64·9 Cals. at constant press. A. Berkenheim discussed the heat of formation. J. J. and F. de Elhuyar, and H. E. Roscoe said that tungsten trioxide turns green when exposed to direct sunlight, probably, added L. Gmelin, because the organic particles and dust diffused in air may exert a reducing action, so that a small portion of the blue oxide becomes mixed with the yellow trioxide. A. F. Wasiléeff found that tungstic acid in the presence of certain reducing agents —*e.g.* cellulose—is reduced by exposure to light. A. Riche observed that if the purified trioxide be confined under purified water for 14 days while exposed to direct sunlight, no green coloration appears. J. A. M. van Liempt also said that light discolours yellow tungsten trioxide ; but N. H. Smith and H. S. Lukens added that any change in colour is only slight, and is superficial. H. M. P. Brinton and A. N. Lohmann added that the effect of sodium salts is negligibly small ; the colour is probably due to traces of impurities like dust. If the ignited trioxide be protected from dust, the light of the mercury vapour lamp has no action, but if it be exposed to the atm., a green colour is developed, and similarly if the trioxide was treated with redistilled ammonia before the ignition. The effect of daylight is negligible in comparison with ultra-violet. A. Karl said that the crystals exhibit **triboluminescence ;** J. Ewles, cathodo-luminescence ; but no ultra-violet fluorescence in X-rays was observed by J. O. Perrine. E. Wrede used tungsten trioxide as a target indicator to determine magnetic separation in a stream of unimolecular hydrogen. C. J. Smithells and H. P. Rooksby's X-ray diffraction pattern is shown in Fig. 14. P. Krishnamurti, and H. Nisi studied the **Raman effect ;** and J. S. Donal, the emission of electrons. J. Vrede observed that the oxide is of no use as a radio-detector.

F. Beijerinck stated that tungstite shows no evidence of **electrical conductivity.** E. Friederich gave $1{\cdot}8 \times 10^9$ ohm per sq. mm. for the resistance. W. Meyer examined the electrical conductivity of compressed rods of the powdered trioxide, and for a rod $0{\cdot}2 \times 0{\cdot}18$ cm. section, and 0·37 cm. long, he gave at room temp. :

Volts .	0·033	0·100	0·200	0·300	0·400	0·666	1·000
Ampères .	$0{\cdot}0_5275$	$0{\cdot}0_5825$	$0{\cdot}0_4166$	$0{\cdot}0_4245$	$0{\cdot}0_4330$	$0{\cdot}0_4541$	$0{\cdot}0_4815$

The **electrolysis** of fused tungstates, and of soln. of tungsten trioxide in various solvents has been discussed in connection with the electrodeposition of tungsten. L. Andrieux electrolyzed a soln. of the oxide in fused boric acid. O. Collenburg and J. Backer found that at a platinum cathode, soln. of alkali tungstates in conc. hydrochloric acid (containing the oxychloride WO_2Cl_2) are reduced quantitatively to derivatives of quinquevalent tungsten, whereas reduction proceeds further at a mercury, lead, or tin cathode. Above 16°, sodium tungstate gives quantitative yields of tervalent tungsten derivatives at the base metal cathode, but below 16°, reduction is not so complete; potassium tungstate is completely reduced only at a lead cathode. During reduction, the colour of the soln. changes first to blue when the tungsten is in the quinquevalent form, and this colour slowly fades on further reduction, yielding eventually a yellowish-green or red soln. of tervalent tungsten. The yellowish-green soln. is always obtained above 35°; it contains compounds of the type $R'_3W_2Cl_9$. The red soln. is obtained at 16° and contains compounds of the type $R'_2(WCl_5.H_2O)$ which are unstable, changing on keeping or warming to compounds of the first-named type. According to O. Collenburg and K. Wilson, electrolysis of soln. containing 11·2 grms. of potassium tungstate and 16 grms. of oxalic acid in 100 c.c. at a current density of 0·01–0·03 amp. per sq. dm. and a temp. of not less than 70° with lead or tin cathodes leads to a complete reduction of tungsten to the quinquevalent stage and no further. The method is well adapted to the preparation of quinquevalent tungsten compounds. K. Fischbeck and E. Einecke found that when used as anode in the electrolysis of 2 per cent. sulphuric acid, tungsten trioxide is reduced to the blue oxide. A. M. Iléeff studied the **thermoelectric force** of powdered tungsten trioxide. E. Wedekind and C. Horst found the **magnetic susceptibility** to be $0·808 \times 10^{-6}$ mass units at 15°; S. Berkman and H. Zocher gave $0·20 \times 10^{-6}$ mass units. S. Freed and C. Kesper studied the subject.

G. C. Gmelin[3] discussed the physiological action of salts of tungstic acid. Tungsten trioxide is more stable and less readily reduced than the corresponding trioxide of molybdenum or chromium. It is an acid anhydride forming tungstic acid with water. The acid and its anhydride were shown by O. W. Gibbs, and J. C. G. de Marignac to have a tendency to form complexes with phosphoric, silicic, boric, and other acids; and by C. Friedheim, to have a tendency to form condensation products. In illustration, the oxides of phosphorus, arsenic, antimony, and bismuth unite with tungsten to form complex salts; aluminium, manganese, iron, chromium, nickel, cobalt, praseodymium, neodymium, lanthanum, and cerium also form a series of tungstates. T. G. y Arnal discussed the reactions of tungstates with various salts.

J. J. Berzelius[4] observed that **hydrogen** reduces heated tungsten trioxide in stages, forming first a blue oxide, then a brown oxide, and then the metal. The observations of G. Chaudron and of L. Wöhler and W. Prager, L. Wöhler and O. Balz, L. Wöhler and R. Günther, W. Reinders and A. W. Vervloet, and H. Altherthum and F. Koref, on this reaction have been discussed in connection with the blue oxide, and with the metal. E. W. Engle said that reduction commences at 620° and is rapid at 950°. C. W. Davis said that the mixture of brown oxides is obtained at 800°–900°, and at 1080°, the metal itself is formed. The reaction was studied by Z. Shibata. J. N. Pearce and M. J. Rice studied the adsorption of water vapour by the oxide. C. Reichard observed that nascent hydrogen, from zinc and dil. hydrochloric or sulphuric acid with tungsten trioxide in suspension, gives a pale blue coloration which gradually becomes darker. F. Wöhler said that the reduction under these conditions proceeds to the blue or violet oxide, and finally to copper-red tungsten dioxide; and O. F. van der Pfordten also gave the dioxide as the end-stage of the reduction by zinc and acid. E. T. Allen and V. H. Gottschalk found that the reduction does not occur with aluminium in alkaline soln. J. J. and F. de Elhuyar found that the oxide is insoluble in **water;** and A. Riche, that it can be exposed to direct sunlight while under water without losing its colour. If rubbed to a fine powder with water, part of it passes through filter-paper as a turbid liquid—*vide infra*, colloidal tungsten trioxide. Tungsten trioxide is tasteless, and if it has been ignited, it does not redden blue litmus. The hydrates are discussed below. T. Fairley found that tungsten trioxide is converted into a higher oxide by **hydrogen dioxide.** B. Kellner said that the freshly-precipitated trioxide is easily soluble in hydrogen dioxide, but when dried it is only partially soluble ; and after ignition, it is insoluble—*vide infra*, pertungstic acid. A. Lottermoser said that hydrogen dioxide is catalytically decomposed in the presence of tungstic acid in accord with the equation $dx/dt=kx(a-x)$. This is due to the rapid formation of *tungsten trioxide hydroperoxide*, $WO_3.H_2O_2$. The photochemical decomposition of the dioxide and dextrose with tungstic acid as a catalyst was studied by J. C. Ghosh and J. Mukherjee.

According to A. Riche, when the trioxide is heated with **chlorine,** a yellow dioxydichloride is formed ; but an analogous reaction with **bromine,** or with **iodine** does not occur. R. Wasmuht studied the reaction with chlorine and the heated trioxide. K. Fredenhagen and G. Cadenbach said that the trioxide is not dissolved or changed by liquid **hydrogen fluoride.** A. Michael and A. Murphy found that a soln. of chlorine in carbon tetrachloride attacks the trioxide at 240°, forming $WOCl_4$, and at 280°, WCl_6. O. Ruff and H. Krug found that the trioxide is attacked with incandescence by **chlorine trifluoride.** H. Copaux found that some tungsten is lost by volatilization when the trioxide is heated in **hydrogen chloride** at 500°, and V. I. Spitzin and L. Kaschtanoff said that the dioxychloride commences to form at 300°. J. J. Berzelius observed that tungsten trioxide which has been ignited is sparingly soluble in **hydrofluoric acid ;** and A. Riche found that it dissolves in conc. hydrofluoric acid at 50° to 60°, forming an oxyfluoride. W. K. van Haagen and E. F. Smith said that hydrofluoric acid has scarcely any action on the trioxide. The ignited trioxide is insoluble in **hydrochloric acid.** A. Pinagel found that no tungsten is lost by volatilization when the trioxide is heated with a mixture of hydrofluoric and hydrochloric acids. E. T. Allen and V. H. Gottschalk found that the trioxide is reduced when it is heated with fuming **hydriodic acid** in a sealed tube at 200°. According to H. O. Schulze, almost all **chlorides** are decomposed when heated with tungsten trioxide in the presence of oxygen, tungstates are formed, and chlorine is evolved. If heated with calcium chloride in the absence of air, the reaction is symbolized : $CaCl_2+2WO_3=CaWO_4+WO_2Cl_2$. The chlorides of magnesium, iron, cobalt, and nickel behave similarly, but not the alkali chlorides. The chlorides of lead and silver are decomposed. L. and H. H. Kahlenberg found that tungsten trioxide and tungstic acid are soluble in fused alkali chlorides ; 100 grms. of fused sodium chloride will dissolve 21·3 grms. of the trioxide ; some chlorine is evolved during the reaction, and when the mass is cooled, most of it dissolves in water, but a little white powder remains undissolved. The reaction is symbolized : $2WO_3+2NaCl=Na_2O.W_2O_5+Cl_2$. If the hydrated trioxide be employed, 100 grms. of fused sodium chloride dissolve 95·7 grms. H_2WO_4 with the evolution of hydrogen chloride, forming $Na_2O.4WO_3$, or $Na_2O.5WO_3$. Tungsten trioxide is also dissolved by other fused **alkali halides.** H. O. Schulze found that potassium iodide is decomposed by tungsten trioxide ; and if an excess of the trioxide be employed, in air, all the iodine is expelled and a tungstate is formed. According to W. R. E. Hodgkinson and F. K. S. Lowndes, if a little tungsten trioxide be placed on molten **potassium chlorate,** oxygen mixed with so much chlorine is evolved that the gas is yellow. G. J. Fowler and J. Grant added that the trioxide lowers the temp. of decomposition of the chlorate, the oxygen is accompanied by chlorine, and some potassium tungstate is formed. G. Bredig discussed tungsten trioxide as a catalytic agent.

J. J. and F. de Elhuyar found that when a mixture of tungsten trioxide and **sulphur** is heated, the blue oxide is formed, or, according to A. Riche, tungsten sulphide, and if alkalies are present, an alkali sulphotungstate is produced. J. J. Berzelius said that the conversion of the heated trioxide by sulphur vapour into sulphide is incomplete ; **hydrogen sulphide** also converts the heated trioxide into sulphide ; and, according to A. Riche, **carbon disulphide** also forms the sulphide. J. J. Berzelius found that the sulphide is formed when the trioxide is heated with **mercuric sulphide.** According to E. F. Smith and H. Fleck, tungsten trioxide, wolframite, or scheelite, forms a red soln. of the oxytetrachloride when treated with **sulphur monochloride.** The trioxide obtained by heating ammonium tungstate, or the trioxide which has been heated for some time in the air, is not completely acted on by sulphur chloride, whereas the trioxide obtained by heating the oxychloride is practically all dissolved by it. This difference is not due to the presence of a nitride or oxynitride. R. D. Hall found that the vapour of sulphur monochloride passed over the heated trioxide forms the volatile oxychloride ; and F. Bourion, that a mixture of chlorine with sulphur chloride transforms the trioxide at 230°–250° completely into a mixture of tungsten oxytetrachloride and dioxydichloride, but not into the hexachloride. G. Darzens and F. Bourion found that **thionyl chloride** attacks tungsten trioxide at 150°, forming the oxytetrachloride, and as the temp. rises the proportion of the accompanying dioxydichloride increases—the hexachloride is not formed. P. Berthier found that **sulphurous acid** has no action, and E. T. Allen and V. H. Gottschalk found that it is not reduced by sulphurous acid in a sealed tube at 200°. E. D. Desi observed that tungsten trioxide is not dissolved even by cold or boiling dil. or conc. **sulphuric acid,** under conditions where molybdenum trioxide is rapidly dissolved. P. Berthier observed that when the trioxide is melted with **potassium hydrosulphate,** and the cold product is leached with water, the undecomposed hydrosulphate is first removed, and normal potassium tungstate then passes into soln. F. J. Faktor observed that when the trioxide is triturated with anhydrous **sodium thiosulphate,** the mixture becomes greenish-yellow, and when heated, tungsten disulphide is formed. O. Brunck found that in acid soln., the trioxide is reduced by **sodium hyposulphite.**

According to A. Riche, aq. **ammonia,** especially in conc. soln., dissolves tungsten trioxide forming a tungstate. A. Rosenheim and F. Jacobsohn found that liquid ammonia does not dissolve a perceptible amount of the trioxide either at ordinary temp. or at 108°–109°. According to F. Wöhler, ammonia converts tungsten trioxide at a dull red-heat into a complex oxynitride, and at a higher temp., into the metal. C. H. Ehrenfeld also observed that complex oxynitrides are formed by the action of ammonia. E. D. Desi also found that **ammonium chloride** mixed with tungsten trioxide, and strongly heated out of contact with air, forms the metal, but at a lower temp. a complex oxynitride is formed. E. T. Allen and V. H. Gottschalk observed that **hydroxylamine** in alkaline soln. does not reduce tungsten trioxide ; and T. Curtius and F. Schrader, that **hydrazine hydrate** forms an indigo-blue mass with the evolution of very little oxygen. P. Sabatier and J. B. Senderens found that the trioxide at 500° is not attacked by **nitric oxide ;** and J. J. Berzelius, that the trioxide is insoluble in **nitric acid,** and in **aqua regia.** C. H. Ehrenfeld observed that the trioxide is reduced to the blue oxide by phosphine at 125°–150°. A. Michaelis found that **phosphorus trichloride** at 200° colours the trioxide superficially green, but no other change was observed ; N. Teclu, C. F. Gerhardt, H. Schiff and A. Piutti, J. Persoz, and C. H. Ehrenfeld observed that **phosphorus pentachloride** furnishes tungsten hexachloride and some complex products. J. Persoz and N. Bloch obtained *tungsten trioxyphosphopentachloride,* $WO_3.PCl_3$—*vide* phosphorus pentachloride, **8**. 50, 32. C. H. Ehrenfeld said that **arsine** acts like phosphine but more sluggishly. L. Gugliamelli studied the complexes of tungstic acid with **arsenic acid ;** and A. Wolff, the complexes with **arsenious, antimonious,** and **phosphorous acids.**

H. N. Warren found that the trioxide is easily reduced by **silicon,** but L. Kahlenberg and W. J. Trautmann were unable to confirm this—any reduction is very local. The reduction of tungsten trioxide to the metal by heating it with **carbon** was observed by J. J. and F. de Elhuyar, A. Riche, C. F. Bucholz, E. G. A. Street, etc. and has been discussed in connection with the metal. H. Moissan said that a carbide is formed. C. Matignon noted the formation of a carbide at about 2000°. H. N. Warren found that **calcium carbide** reduces the trioxide to the metal. As in the case of hydrogen, W. Fränkel found that the reduction of tungsten trioxide by **carbon monoxide** takes place in stages: $2WO_3+CO=CO_2+W_2O_5$, has an equilibrium constant $K=[CO_2]/[CO]$ has between 17·2 and 21·1 between 750° and 1050°; and for the stage $W_2O_5+CO\rightleftharpoons 2WO_2+CO_2$ at 800°, $K=5{\cdot}08$; the last stage $WO_2+2CO\rightleftharpoons W+2CO_2$ could not be measured because of the formation of carbide. Z. Shibata also studied the reaction; he found that $\log K_p=1555{\cdot}5T^{-1}-1{\cdot}1427$ for the reaction $2WO_3+CO=W_2O_5+CO_2$; $\log K_p=1029{\cdot}8T^{-1}-0{\cdot}7884$ for the reaction $W_2O_5+CO=2WO_2+CO_2$; and $\log K_p=321{\cdot}6T^{-1}-0{\cdot}0647$ for $\frac{1}{2}WO_2+CO=\frac{1}{2}W+CO_2$. According to C. H. Ehrenfeld, **methane** does not reduce the trioxide heated by a bunsen burner, but at a higher temp. the dioxide is formed; no reduction occurred with **ethane,** but at a red-heat, **ethylene** furnishes the blue oxide; and **acetylene,** the blue and brown oxides. E. D. Desi also observed the formation of the blue oxide with ethylene, and he found that with cyanogen, a complex oxynitride is formed; and that fused **potassium cyanide** forms a complex oxynitride, and at a very high temp., silver-white globules of tungsten. F. Göbel found that **carbon monoxide** reduces the heated trioxide to the blue oxide. P. Camboulives observed that when the trioxide is heated to 560° in the vapour of **carbon tetrachloride,** an oxychloride is formed, and A. Michael and A. Murphy said that no reaction occurs at 240°, but at 280°, the hexachloride is produced—in the presence of chlorine, the oxychloride is formed at 240°, and the hexachloride at 280°. P. Sabatier and A. Mailhe, and J. N. Pearce and A. M. Alvarado studied the catalytic action of the trioxide on **alcohol** vapour whereby the alcohol is reduced to ethylene. J. N. Pearce and M. J. Rice studied the adsorption of the vapour of ethyl alcohol, ethyl acetate, and of acetic acid at 99·4°; and S. Ghosh and A. K. Bhattacharya, the photochemical reduction of tungstic acid by ethyl alcohol; and J. C. Ghosh and S. K. Nandy, of formaldehyde. J. C. Ghosh and J. Mukherjee, and E. T. Allen and V. H. Gottschalk found that the trioxide is not reduced by alcohol or **oxalic acid** with hot conc. hydrochloric acid; nor is it reduced by **grape-sugar.** The trioxide is reduced to the blue oxide by boiling **acetic acid** and other **organic compounds.** L. Fernandes studied the compounds formed with gallic acid; R. F. Weinland and co-workers, the action of the phenols, and phenolic acids; A. V. Dumansky and S. I. Dyachkovsky studied the action of tartaric acid. According to A. C. Neish, *m*-nitrobenzoic acid does not give a precipitate with soln. of ammonium tungstate; according to G. von Knorre, benzidine hydrochloride precipitates the tungsten quantitatively from cold soln. of the tungstates; and, according to M. Tschilikin, α-naphthylamine gives a quantitative precipitation. E. F. Smith studied the action of organic bases.

J. L. Gay Lussac and L. J. Thénard found that **potassium** or **sodium** when heated reduces tungsten trioxide vigorously with *une lumière vive.* E. D. Desi also reduced the trioxide with sodium; and with magnesium he obtained an alloy of tungsten. The reducing action of these and other **metals** has been discussed in connection with the preparation of tungsten (*q.v.*). O. Freih found that zinc reduces tungstic acid to the dioxide. K. Someya reduced tungsten trioxide to the quadrivalent stage by bismuth amalgam, and to the tervalent stage by lead, cadmium, and zinc amalgams. For the action of various basic oxides, *vide infra,* the tungstates. A. Riche found that conc. soln. of the **alkali hydroxides or carbonates** readily dissolve the trioxide, forming soln. of the tungstates; similarly also with the fused alkalies. E. J. Mills and D. Wilson measured what they called the chemical effect of tungsten trioxide when it is fused with potassium carbonate. This was expressed in terms of the units, a, of carbon dioxide evolved per unit of the trioxide acting for an hour at 750°. They found for tungsten trioxide, $a=0{\cdot}99597$; for silicon dioxide, $a=0{\cdot}83$; and for titanic oxide, $a=0{\cdot}71917$, showing that the action of titanic oxide is more sluggish than silica, and silica is more sluggish than tungsten trioxide. The blue colour obtained by the action of warm **stannous**

chloride on tungsten trioxide has been previously described. K. Someya described the reduction of tungstic acid or its salts with the amalgams of calcium, zinc, and lead.

REFERENCES.

[1] B. Silliman, *Amer. Journ. Science*, (1), **4**. 52, 1822 ; J. B. Scrivenor and J. C. Shenton, *ib.*, (5), **13**. 487, 1927 ; J. D. Dana, *A System of Mineralogy*, New York, 186, 1868 ; 202, 1898 ; F. S. Beudant, *Traité élémentaire de minéralogie*, Paris, **2**. 659, 1832 ; R. P. Greg and W. G. Lettsom, *Manual of the Mineralogy of Great Britain and Ireland*, London, 350, 1858 ; C. C. von Leonhard, *Handbuch der Oryktognosie*, Heidelberg, 345, 1826 ; E. F. Glocker, *Handbuch der Mineralogie*, Nürnberg, 563, 1831 ; *Generum et specierum mineralium secundum ordines naturales digestorum synopsis*, Halie, 66, 1847 ; W. Phillips, *Introduction to Mineralogy*, London, 254, 1823 ; F. von Kobell, *Charakteristik der Mineralien*, Nürnberg, **2**. 35, 1831 ; A. Lacroix, *Minéralogie de la France et de ses colonies*, Paris, **3**. 10, 1901 ; F. D. Smith, *Zeit. prakt. Chem.*, **10**. 314, 1902 ; V. R. von Zepharovich, *Mineralogisches Lexicon für das Kaiserthum Oesterreich*, Wien, 1859 ; J. J. Berzelius, *Arsber. Physik Kemi*, 140, 1823 ; J. H. Collins, *A Handbook to the Mineralogy of Cornwall and Devon*, London, 107, 1876 ; W. F. Petterd, *Catalogue of the Minerals of Tasmania*, Hobart, 93, 1896 ; P. A. Dufrénoy, *Traité de minéralogie*, Paris, 520, 1856.

[2] I. Langmuir, *Journ. Amer. Chem. Soc.*, **35**. 105, 1913 ; F. A. Bernoulli, *Pogg. Ann.*, **111**. 573, 1860 ; *Chem. News*, **5**. 116, 1862 ; J. Waddell, *Amer. Chem. Journ.*, **8**. 280, 1886 ; *Chem. News*, **55**. 101, 112, 1887 ; *Trans. Roy. Soc. Edin.*, **33**. 1, 1889 ; *Zeit. phys. Chem.*, **3**. 491, 1889 ; E. Zettnow, *Pogg. Ann.*, **130**. 16, 241, 1867 ; A. E. Nordenskjöld, *ib.*, **114**. 612, 1861 ; *Oefvers. Akad. Förh.*, **17**. 300, 1860 ; A. Safarik, *Sitzber. Akad. Wien*, **47**. 246, 1863 ; E. D. Clark, *The Gas Blowpipe*, London, 79, 1819 ; H. Debray, *Compt. Rend.*, **55**. 287, 1862 ; A. Karl, *ib.*, **146**. 1104, 1908 ; C. Matignon, *ib.*, **177**. 1290, 1923 ; L. Gmelin, *Handbook of Chemistry*, London, **4**. 28, 1850 ; H. E. Roscoe, *Liebig's Ann.*, **162**. 359, 1872 ; *Proc. Manchester Lit. Phil. Soc.*, **11**. 79, 1872 ; *Chem. News*, **25**. 51, 73, 90, 1873 ; *Bull. Soc. Chim.*, (2), **25**. 61, 1873 ; H. Copaux, *Bull. Soc. Min.*, **29**. 83, 1906 ; J. J. and F. de Elhuyar, *Análisis quimico del volfram y exámen de un nuovo metal que entra en su composicion*, Bascongada, 1783 ; *A Chemical Examination of Wolfram and Examination of a New Metal which enters into its Composition*, London, 1785 ; *Chemische Zerkliederung des Wolframs*, Halle, 1786 ; *Mém. Acad. Toulouse*, **2**. 141, 1784 ; J. B. A. Dumas, *Ann. Chim. Phys.*, (3), **55**. 143, 1859 ; E. F. Smith and F. F. Exner, *Proc. Amer. Phil. Soc.*, **43**. 123, 1904 ; *Chem. News*, **90**. 37, 49, 66, 1904 ; *Journ. Amer. Chem. Soc.*, **26**. 1082, 1904 ; A. Riche, *Ann. Chim. Phys.*, (3), **50**. 33, 1857 ; S. M. Delépine, *Études des réactions réversibles de l'hydrogène et de l'oxyde de carbone sur les oxydes métalliques*, Paris, 1921 ; *Compt. Rend.*. **131**. 184, 1900 ; *Bull. Soc. Chim.*, (3), **23**. 675, 1900 ; G. A. Meerson, *Journ. Russ. Phys. Chem. Soc.*, **60**. 1217, 1928 ; S. M. Delépine and L. A. Hallopeau, *Compt. Rend.*, **129**. 600, 1899 ; C. J. B. Karsten, *Schweigger's Journ.*, **65**. 394, 1832 ; W. Herapath, *Phil. Mag.*, (1), **64**. 321, 1824 ; J. Ewles, *ib.*, (6), **45**. 957, 1923 ; H. Schröder, *Liebig's Ann.*, **172**. 278, 1874 ; **173**. 71, 1874 ; **174**. 249, 1874 ; H. Kopp, *Liebig's Ann. Suppl.*, **3**. 1, 1864 ; W. G. Mixter, *Amer. Journ. Science*, (4), **26**. 125, 1908 ; H. V. Regnault, *Ann. Chim. Phys.*, (3), **1**. 129, 1841 ; A. S. Russell, *Phys. Zeit.*, **13**. 59, 1912 ; J. N. Pearce and A. M. Alvarado, *Journ. Phys. Chem.*, **29**. 256, 1925 ; A. A. Read, *Journ. Chem. Soc.*, **65**. 313, 1894 ; C. J. Smithells and H. P. Rooksby, *ib.*, 1882, 1927 ; E. Wedekind and C. Horst, *Ber.*, **48**. 105, 1915 ; J. A. M. van Liempt, *Rec. Trav. Chim. Pays-Bas*, **43**. 30, 1924 ; *Chem. News*, **132**. 357, 1926 ; *Zeit. anorg. Chem.*, **119**. 310, 1921 ; **127**. 215, 1923 ; H. C. Burger, *ib.*, **121**. 240, 1922 ; L. Weiss, *ib.*, **65**. 334, 1910 ; V. I. Spitzin and L. Kaschtanoff, *Journ. Russ. Phys. Chem. Soc.*, **58**. 1230, 1926 ; *Zeit. anorg. Chem.*, **157**. 141, 1926 ; F. M. Jäger and H. C. Germs, *ib.*, **119**. 145, 1921 ; H. C. Germs, *De thermische Analyse van Loodsulfaat, -Chromaat, -Molybdaat, -Wolframaat en van hun Binaire Combinaties*, Groningen, 1917 ; H. Alterthum and F. Koref, *Zeit. Elektrochem.*, **31**. 508, 1925 ; F. Born, *ib.*, **31**. 309, 1925 ; N. H. Smith and H. S. Lukens, *Chem. News*, **132**. 33, 1926 ; H. M. P. Brinton and A. N. Lohmann, *ib.*, **133**. 275, 1926 ; W. R. Mott, *Trans. Amer. Electrochem. Soc.*, **34**. 255, 1918 ; F. Beijerinck, *Neues Jahrb. Min. B.B.*, **11**. 460, 1897 ; J. E. Moose and S. W. Parr, *Journ. Amer. Chem. Soc.*, **46**. 2656, 1924 ; A. M. Iléeff, *Journ. Russ. Phys. Chem. Soc.*, **40**. 220, 1908 ; A. F. Wasiléeff, *ib.*, **44**. 819, 1912 ; L. Wöhler and R. Günther, *Zeit. Elektrochem.*, **29**. 276, 1923 ; A. Pinagel, *Beiträge zur Kenntis der Wolframate und Silicowolframate*, Bern, 10, 1904 ; D. Balareff, *Journ. prakt. Chem.*, (2), **102**. 283, 1921 ; E. Friederich, *Zeit. Physik*, **31**. 813, 1925 ; E. Wrede, *ib.*, **41**. 569, 1927 ; J. O. Perrine, *Phys. Rev.*, (2), **22**. 48, 1923 ; O. Collenberg and K. Wilson, *Zeit. Elektrochem.*, **31**. 555, 1925 ; O. Collenberg and J. Backer, *ib.*, **30**. 230, 1924 ; W. D. Bancroft and H. B. Weiser, *Journ. Phys. Chem.*, **18**. 213, 1914 ; S. Berkman and H. Zocher, *Zeit. phys. Chem.*, **124**. 318, 1926 ; K. Fischbeck and E. Einecke, *ib.*, **130**. 21, 1927 ; A. Berkenheim, *ib.*, **135**. 231, 1928 ; C. del Fresno, *Anal. Fis. Quim.*, **24**. 707, 1926 ; W. Meyer, *Ueber die elektrische Leitfähigkeit einer Reihe chemischer Verbindungen in festem Zustand*, Berlin, 1926 ; F. M. Jäger and E. Rosenbohm, *Versl. Akad. Amsterdam*, **36**. 763, 1927 ; A. Riebeth, *Plastische Massen mit verschiedenen anorganischen Stoffen und die Möglichkeiten ihrer keramischen Verwertung*, Breslau, 1927 ; O. Ruff and A. Reibeth, *Zeit. anorg. Chem.*, **173**. 373, 1928 ; Z. Shibata, *Tech. Rep. Tohoku*, **8**. 129, 145, 1929 ; S. Freed and C. Kasper, *Journ. Amer. Chem. Soc.*, **52**. 4671, 1930 ; P. Niggli, *Zeit. Kryst.*, **75**. 254, 1930 ; H. Nisi, *Japan. Journ. Phys.*, **5**. 119, 1929 ; J. Maydel,

Zeit. anorg. Chem., **186**. 289, 1930 ; W. Biltz, *ib.*, **193**. 321, 1930 ; P. Krishnamurti, *Indian Journ. Phys.*, **5**. 633, 1930 ; J. S. Donal, *Phys. Rev.*, (2), **36**. 1172, 1930 ; L. Andrieux, *Recherches sur l'electrolyse des oxydes métalliques dissoux dans l'anhydride borique ou dans les borates fondus*, Paris, 1929 ; *Ann. Chim. Phys.*, (10), **12**. 423, 1929 ; J. Vrede, *Phys. Zeit.*, **31**. 323, 1930 ; H. P. Walmsley, *Phil. Mag.*, (7), **7**. 1097, 1929 ; Y. Nakazawa and T. Okada, *Elect. Rev.*, **17**. 89, 1928.

[3] G. C. Gmelin, *Schweigger's Journ.*, **43**. 110, 1825 ; *Edin. Journ. Med.*, **3**. 324, 1827 ; O. W. Gibbs, *Amer. Chem. Journ.*, **2**. 217, 281, 1880 ; C. Friedheim, *Zeit. anorg. Chem.*, **6**. 30, 1894 ; J. C. G. de Marignac, *Ann. Chim. Phys.*, (3), **69**. 5, 1863 ; T. G. y Arnal, *Anal. Soc. Fis. Quim.*, **26**. 435, 1928.

[4] J. L. Gay Lussac and L. J. Thénard, *Recherches physicochimiques*, Paris, **1**. 317, 1811 ; C. Reichard, *Chem. Ztg.*, **27**. 1, 1903 ; J. B. Trommsdorf, *Trommsdorf's Journ.*, **20**. 94, 1911 ; F. Wöhler, *Gött. Nachr.*, 35, 1850 ; *Liebig's Ann.*, **73**. 190, 1850 ; *Ann. Chim. Phys.*, (3), **29**. 187, 1850 ; A. Riche, *ib.*, (3), **50**. 33, 1857 ; J. J. Berzelius, *Schweigger's Journ.*, **16**. 476, 1816 ; *Ann. Phil.*, **3**. 245, 1814 ; *Ann. Chim. Phys.*, (2), **17**. 13, 1821 ; *Pogg. Ann.*, **4**. 147, 1825 ; **8**. 147, 267, 1826 ; J. J. and F. de Elhuyar, *Análisis quimico de volfram y exámen de un nuovo metal que entra en su composicion*, Bascongada, 1783 ; *A Chemical Examination of Wolfram and Examination of a New Metal which enters into its Composition*, London, 1785 ; *Chemische Zerkliederung des Wolframs*, Halle, 1786 ; *Mém. Acad. Toulouse*, **2**. 141, 1784 ; O. F. von der Pfordten, *Liebig's Ann.*, **222**. 159, 1884 ; O. Brunck, *ib.*, **336**. 281, 1905 ; G. Rauter, *ib.*, **270**. 236, 1892 ; H. Schiff and A. Piutti, *Gazz. Chim. Ital.*, **9**. 277, 1879 ; H. Schiff, *Liebig's Ann.*, **117**. 94, 1861 ; **197**. 185, 1879 ; N. Teclu, *ib.*, **187**. 255, 1877 ; H. Alterthum and F. Koref, *Zeit. Elektrochem.*, **31**. 508, 1925 ; H. N. Warren, *Chem. News*, **64**. 75, 1891 ; **75**. 2, 1897 ; W. R. E. Hodgkinson and F. K. S. Lowndes, *ib.*, **58**. 309, 1888 ; L. P. Wyman, *The Purification of Tungstic Acid*, Philadelphia, 1902 ; C. H. Ehrenfeld, *Bull. Soc. Chim.*, (3), **14**. 919, 1895 ; *Journ. Amer. Chem. Soc.*, **17**. 381, 1895 ; E. D. Desi, *ib.*, **19**. 213, 1897 ; W. K. van Haagen and E. F. Smith, *ib.*, **33**. 1504, 1911 ; R. D. Hall, *ib.*, **26**. 1244, 1904 ; E. F. Smith and H. Fleck, *ib.*, **21**. 1008, 1900 ; A. C. Neish, *ib.*, **26**. 787, 1904 ; E. G. A. Street, *Monit. Scient.*, (4), **9**. 623, 1895 ; J. Persoz, *Ann. Chim. Phys.*, (4), **1**. 93, 1864 ; *Compt. Rend.*, **58**. 1196, 1864 ; J. Persoz and N. Bloch, *ib.*, **28**. 86, 289, 1849 ; H. Moissan, *ib.*, **125**. 839, 1897 ; *Le four électrique*, Paris, 232, 1897 ; London, 160, 1904 ; *Ann. Chim. Phys.*, (7), **19**. 302, 1896 ; P. Sabatier and J. B. Senderens, *Compt. Rend.*, **114**. 1429, 1892 ; **115**. 236, 1892 ; **120**. 618, 1895 ; *Bull. Soc. Chim.*, (3), **13**. 870, 1895 ; *Ann. Chim. Phys.*, (7), **7**. 348, 1896 ; P. Berthier, *Traité des essais par la voie sèche*, Paris, **2**. 65, 1834 ; *Ann. Mines*, (3), **3**. 39, 1833 ; *Ann. Chim. Phys.*, (2), **4**. 44, 1834 ; (3), **7**. 74, 1843 ; G. Darzens and F. Bourion, *ib.*, (8), **21**. 88, 1910 ; J. C. Ghosh and J. Mukherjee, *Journ. Indian Chem. Soc.*, **6**. 231, 1929 ; J. N. Pearce and M. J. Rice, *Journ. Phys. Chem.*, **33**. 692, 1929 ; Z. Shibata, *Tech. Rep. Tohoku*, **8**. 129, 145, 255, 271, 1929 ; F. Bourion, *Compt. Rend.*, **153**. 271, 1911 ; P. Sabatier and A. Mailhe, *Ann. Chim. Phys.*, (8), **20**. 289, 1910 ; *Chem. Ztg.*, **31**. 642, 1907 ; **35**. 485, 507, 1911 ; H. E. Quantin, *Compt. Rend.*, **104**. 223, 1887 ; **106**. 1074, 1888 ; C. Matignon, *ib.*, **77**. 1290, 1923 ; P. Camboulives, *ib.*, **150**. 175, 1910 ; S. M. Delépine, *ib.*, **131**. 184, 1900 ; E. Defacqz, *ib.*, **123**. 308, 1896 ; G. Chaudron, *ib.*, **170**. 1056, 1920 ; *Études des réactions réversibles de l'hydrogène et de l'oxyde de carbone sur les oxydes métalliques*, Paris, 1921 ; G. J. Fowler and J. Grant, *Journ. Chem. Soc.*, **57**. 272, 1890 ; T. Fairley, *ib.*, **31**. 125, 1877 ; E. J. Mills and D. Wilson, *ib.*, **33**. 360, 1878 ; *Chem. News*, **37**. 240, 1878 ; H. O. Schulze, *Journ. prakt. Chem.*, (2), **21**. 437, 441, 1880 ; F. Göbel, *ib.*, (1), **6**. 386, 1835 ; *Bull. Soc. Nat. Moscow*, **9**. 312, **1086** ; A. Michaelis, *Jena Zeit.*, **7**. 110, 1871 ; F. J. Faktor, *Pharm. Post.*, **38**. 527, 1905 ; G. Bredig, *Zeit. Biochem.*, **6**. 283, 1907 ; L. and H. H. Kahlenberg, *Trans. Amer. Electrochem. Soc.*, **46**. 181, 1924 ; L. Kahlenberg and W. J. Trautmann, *ib.*, **39**. 377, 1921 ; F. Schrader, *Metalldoppelsalze des Diammoniums und Diamids*, Kiel, 1893 ; T. Curtius and F. Schrader, *Journ. prakt. Chem.*, (2), **50**. 311, 1894 ; E. W. Engle, *Trans. Amer. Electrochem. Soc.*, **51**. 345, 1927 ; A. Pinagel, *Beiträge zur Kenntnis der Wolframate und Silicowolframate*, Bern, 52, 1904 ; B. Kellner, *Untersuchungen über Perwolframate*, Berlin, 1909 ; H. Copaux, *Bull. Soc. Min.*, **29**. 83, 1906 ; C. W. Davis, *Journ. Ind. Eng. Chem.*, **11**. 201, 1919 ; A. Michael and A. Murphy, *Amer. Chem. Journ.*, **44**. 365, 1910 ; E. T. Allen and V. H. Gottschalk, *ib.*, **27**. 328, 1902 ; A. Rosenheim and F. Jacobsohn, *Zeit. anorg. Chem.*, **50**. 297, 1906 ; G. Jander and D. Mojert, *ib.*, **175**. 270, 1928 ; J. A. M. van Liempt, *ib.*, **126**. 183, 226, 1923 ; R. F. Weinland, A. Babel, K. Gross and H. Mai, *ib.*, **150**. 177, 1926 ; K. Someya, *ib.*, **138**. 291, 1924 ; **145**. 168, 1925 ; **152**. 368, 1926 ; V. I. Spitzin and L. Kaschtanoff, *ib.*, **157**. 141, 1926 ; *Journ. Russ. Phys. Chem. Soc.*, **58**. 1230, 1926 ; C. F. Gerhardt, *Compt. Rend. Trav. Chim.*, 91, 1850 ; *Compt. Rend.*, **34**. 755, 902, 1852 ; *Ann. Chim. Phys.*, (3), **18**. 204, 1846 ; (3), **37**. 285, 1853 ; (3), **53**. 302, 1858 ; W. Reinders and A. W. Vervloet, *Rec. Trav. Chim. Pays-Bas*, **42**. 625, 1923 ; L. Wöhler and R. Günther, *Zeit. Elektrochem.*, **29**. 276, 1923 ; L. Wöhler and O. Balz, *ib.*, **27**. 406, 1921 ; L. Wöhler and W. Prager, *ib.*, **23**. 199, 1917 ; W. Fränkel, *Festschrift Jahrhundertfeier Inst. Frankfurt a.M.*, 136, 1924 ; L. Fernandes, *Gazz. Chim. Ital.*, **53**. 514, 1923 ; G. von Knorre, *Ber.*, **38**. 783, 1905 ; M. Tschilikin, *ib.*, **42**. 1302, 1909 ; E. F. Smith, *Chem. News*, **137**. 219, 1928 ; A. V. Dumansky and S. I. Dyachkovsky, *Koll. Zeit.*, **48**. 49, 1929 ; A. Lottermoser, *Zeit. Elektrochem.*, **35**. 610, 1929 ; C. Fredenhagen and C. Cadenbach, *Zeit. phys. Chem.*, **146**. 245, 1930 ; S. Ghosh and A. K. Bhattacharya, *Journ. Indian Chem. Soc.*, **7**. 717, 1930 ; J. C. Ghosh and S. K. Nandy, *ib.*, **6**. 975, 1929 ; O. Ruff and H. Krug, *Zeit. anorg. Chem.*, **190**. 270, 1930 ; O. Freih, *Ber.*, **16**. 508, 1883 ; R. Wasmuht, *Zeit. angew. Chem.*, **43**. 98, 125, 1930 ; L. Gugliamelli, *Anal. Farm. Bioquim*, **1**. 66, 1930 ; C. F. Bucholz, *Schweigger's Journ.*, **3**.

1, 1811; J. N. Pearce and A. M. Alvarado, *Journ. Phys. Chem.*, **29**. 256, 1925; A. Wolff, *Zur Kenntnis der Parawolframate und einiger Heteropolywolframate*, Berlin, 1930; A. Rosenheim and A. Wolff, *Zeit. anorg. Chem.*, **193**. 47, 64, 1930.

§ 11. The Hydrates of Tungsten Trioxide—The Tungstic Acids

According to E. Zettnow,[1] and C. D. Braun, when sodium tungstate is treated with hot sulphuric acid, the hydrated tungstic acid which separates contains, after drying at a low temp., variable quantities of water. Thus, when dried at 50°, it has 3·68 per cent. of water—or $2WO_3.H_2O$; at 120° to 130°, 2·46 per cent.—or $3WO_3.H_2O$; and at 200°, 1·74 per cent.—or $4WO_3.H_2O$. The dihydrate dried at 100° to 110° was found by C. D. Braun to correspond with the *hemihydrate*, $2WO_3.H_2O$; and it has been called *pyrotungstic acid*, $H_2W_2O_7$, but there is no evidence to show that this composition is other than an arbitrarily selected stage in the continuation desiccation of an indefinite hydrate, $WO_3.nH_2O$—*vide infra*, Fig. 23.

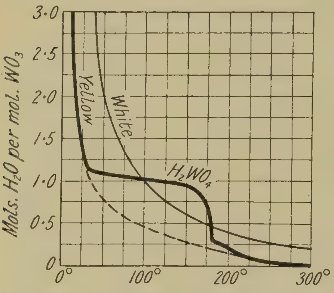


Fig. 23.—Dehydration Curves of the White and Yellow Hydrates of Tungsten Trioxide.

A. Laurent, A. Riche, and V. Forcher decomposed an aq. soln. of a tungstate or metatungstate with an excess of *hot* acid, and dried the product in air, or, according to C. D. Braun, over conc. sulphuric acid. The yellow hydrate was considered to be the *monohydrate*, $WO_3.H_2O$, **tungstic acid.** It was also obtained by decomposing wolframite with aqua regia; and C. D. Braun obtained it by drying the dihydrate over conc. sulphuric acid until its weight was constant. A. Laurent added that the yellow hydrate is stable at 200°; and L. Pissarjewsky, that its heat of neutralization is 13·698 Cals. per mol. The effects produced by acids of different concentration, etc., are discussed in connection with the extraction of tungsten. G. F. Hüttig and B. Kurre recommended the following method for preparing the *yellow tungstic acid*:

Add 20 grms. of purified calcium tungstate to a boiling mixture of 50 c.c. of water, 40 c.c. of conc. hydrochloric acid, and 40 c.c. of conc. nitric acid; wash the yellow precipitate by decantation 8 times with water feebly acidulated with hydrochloric acid; dissolve the precipitate in 50 c.c. of conc. aq. ammonia; and filter. Pour the boiling filtrate into a mixture of 60 c.c. of water, 50 c.c. of nitric acid, and 10 c.c. of hydrochloric acid; wash the yellow tungstic acid many times by decantation with water; filter through Zsigmondy's filter; and stir up the product with water. After the mixture has stood for about 14 days, passing now and again an electric current through the liquid—using platinum electrodes—the tungstic acid will have settled as an emulsion. The excess of water is syphoned off, the emulsion is concentrated on a water-bath. The product is then dried over solid sodium hydroxide. The composition approximates $WO_3.1·13H_2O$.

J. Eltzbacher used a similar process. A. Pinagel transformed sodium tungstate into barium tungstate, by adding barium chloride to a soln. of the sodium salt, and flocculating the precipitate with ammonium nitrate. The product was then decomposed by hot aqua regia, and the yellow hydrate washed with hot water. A. Riche said that if a soln. of the hydrated trioxide in conc. hydrofluoric acid at 50° or 60°, be evaporated in air, the oxyfluoride which first separates is decomposed forming crystals of yellow tungstic acid. A. M. Morely examined the products obtained by different modes of preparation, and found that the X-radiograms indicate the existence of the *monohydrate*, $WO_3.H_2O$, or H_2WO_4, and the *dihydrate*, $WO_3.2H_2O$, or $H_2WO_4.H_2O$. The other products are either condensed compounds or impure substances either non-crystalline or imperfectly crystalline. G. Jander and T. Aden observed the change in the visible and ultra-violet absorption spectra with aggregation in alkaline and acid soln. The yellow hydrate dissolves in water, for R. C. Wells found the sp. conductivity of the aq. soln. to be $10·3\times10^{-6}$ at 25°; he observed very little change when the soln. were left to stand for a long time, hence it is inferred that no large quantity of a polymerized acid is formed under these conditions. J. W. Mallet gave for the solubility in 38 per cent. hydrochloric acid, 0·36 and 0·75 grm. WO_3 per 100 grms. of soln. respectively at 50° and 80°; and R. F. Bernhardi-Grisson, for the solubility in 40 per cent. hydrochloric acid, 44·75 and 53·7 grms. per 100 grms. of soln. respectively at 25° and 50°. The yellow hydrate is readily soluble in alkali-lye.

According to A. Riche, J. J. and F. de Elhuyar, and J. J. Berzelius, if a soln. of a tungstate be treated with *cold* dil. acid, some soluble or metatungstic acid passes into soln., and there is formed a white luminous precipitate which tastes at first sweet and afterwards bitter; reddens litmus; and dissolves in water especially when hot, but scarcely at all in water containing acid. The white product forms yellow tungstic acid when it is boiled with sulphuric, hydrochloric, or nitric acid. When ignited in closed vessels it forms a blue oxide, and in open vessels, yellow tungsten trioxide. E. F. Anthon said that the white precipitate is amorphous, but, according to A. Riche, it becomes crystalline after two or three washings. The white product is very liable to pass through the filter-paper when it is washed. C. W. Scheele regarded the precipitate as pure tungstic acid, but J. J. Berzelius showed that it is always contaminated with some of the acid used as the precipitant; and J. J. and F. de Elhuyar, and J. C. G. de Marignac, with some of the alkali with which the tungstic acid was previously combined. The analyses of A. Riche, E. F. Anthon, C. D. Braun, and V. Forcher, show that the product is a *dihydrate*, $WO_3.2H_2O$. G. F. Hüttig and B. Kurre obtained *white tungstic acid* by the following procedure:

Ten grams of calcium tungstate are treated with acid as indicated above in connection with the yellow acid, and the product mixed with enough conc. aq. ammonia to dissolve nearly all the precipitate. The filtered soln. is cooled by ice, and 70 c.c. of conc. hydrochloric acid added drop by drop. The tungstic acid is filtered off, and again dissolved in conc. aq. ammonia. It is cooled and treated with hydrochloric acid as before, but with the exclusion of light. The mixture is filtered, and the precipitate washed six times with 25 c.c. of water. The white tungstic acid so formed still retains traces of ammonia and hydrochloric acid; and it has a tendency gradually to pass into the yellow variety. The analysis of a sample so prepared contained WO_3, 13·6 per cent.; H_2O, 86·05; NH_4Cl, 0·2; free HCl, 0·15 per cent. It showed no yellow tinge after being kept 14 days.

The white hydrate was also obtained by A. Riche, H. E. Roscoe, and V. Forcher by the action of moist air on tungsten hexachloride, pentachloride, oxytetrachloride, or dioxydichloride. E. F. Anthon, and V. Forcher also said that the white dihydrate is formed when the anhydrous trioxide is rubbed up with water and filtered—the dihydrate passes through the filter-paper forming a turbid filtrate.

According to G. F. Hüttig and B. Kurre, the white acid is to be regarded as hydrated tungsten trioxide because the composition-temp. curve, Fig. 23, shows that the adsorbed water is gradually lost as the temp. is raised, and the curve shows no signs of a break corresponding with the formation of a definite hydrate. The decomposition press., p mm., the decomposition temp., θ°, and the number n mols. of water per mol. of WO_3 were found to be:

p .	10·4	16·6	13·7	15·5	12·0	14·6	12·0	7·6	11·5
θ .	16°	21°	20°	36°	85°	129°	180°	305°	>500°
n .	60·61	44·90	16·0	2·44	0·95	0·64	0·39	0·24	0

The case is different with the yellow hydrate for it shows a definite break, Fig. 23, corresponding with the formation of a monohydrate, $WO_3.H_2O$, or tungstic acid, H_2WO_4. The following is a selection from the observed values of p, θ, and n:

p .	20·5	12·2	8·9	12	8·8	9·8	8·7	8·9	7·6
θ .	16°	17°	13°	20°	22°	94°	120°	218·5	278
n .	12·62	6·61	2·52	1·35	1·21	1·05	1·00	0·07	0·04

At temp. above 188° and below 76°, the white hydrate is the more stable, whereas between 76° and 188°, the yellow variety is the more stable. The subject was investigated by J. A. M. van Liempt. G. F. Hüttig found that yellow tungstic acid, $WO_3.H_2O$, has an X-radiogram showing that the chemically combined water molecules occupy fixed positions in the crystal-lattice ; with zeolites, on the contrary, the greater portion of the water is free to move in the crystal lattice. H. C. Burger found that the X-radiogram of tungsten trioxide is different from that of the monohydrate which has a definite and characteristic crystalline form, and it is on this account to be regarded as a definite compound. A definite compound was also indicated in the case of the dihydrate. Hence, if $W(OH)_6$ be *orthotungstic* acid, H_6WO_6 ; $WO(OH)_4$, is *paratungstic acid*, H_4WO_4, or $WO_3.2H_2O$; and $WO_2(OH)_2$, *metatungstic acid*, H_2WO_4, or $WO_3.H_2O$. This is in accord with the nomenclature in use for iodic and many other acids, but in the case of tungsten the terms metatungstic acid, and paratungstic acid have been employed with a different connotation—*vide infra*—namely, for the parent *paratungstic acid* of the salt with the formula $3Na_2O.7WO_3.21H_2O$, or the alternative $5Na_2O.12WO_3.28H_2O$; and of the parent *metatungstic acid*, of the salt $Na_2O.4WO_3.nH_2O$. For the so-called *isotungstic acid*, *vide supra*, the history of tungsten. M. E. Chevreul, and J. J. and F. de Elhuyar said that tungstic acid possesses a real acidity, for it reddens blue litmus. According to H. T. S. Britton, and H. T. S. Britton and W. L. German, when 100 c.c. of a 0·0678N-NaOH, and 0·0250M-WO_3 are titrated with 0·1020N-HCl, the electrometric curve is that shown in Fig. 24. A sharp diminution in hydrogen-ion concentration occurred when the amount of hydrochloric acid necessary to react with the alkali in excess of that required to form the normal sodium tungstate (Na_2WO_4) was added. This explains the successful use of phenolphthalein as an indicator for the titration of the oxide—observed by O. Hertig, A. Lottermoser and co-workers, D. Mojert, D. D. Peirce and L. F. Yntema, A. Rosenheim and A. Wolff, G. Jander and W. Heukeshoven, S. L. Dyachkovsky, M. L. Holt and L. Kahlenberg, F. Hundeshagen, and S. C. Lind and B. C. Trueblood. Sodium paratungstate with either 2·33 or 2·4 mols of Na_2O per mol of WO_3, respectively in accord with the 3 : 7-formula or the 5 : 12-formula, corresponds with a $H^{\cdot}$-ion conc. of $p_H = 6{\cdot}0$ respectively, and in agreement with H. Schmidt's observation that a soln. of the 2·4 salt is acidic to rosolic acid, and alkaline to cochineal. The metatungstate, $Na_2W_4O_{13}$, is formed when the $H^{\cdot}$-ion conc. is 10^{-4}. The inflexion in the hydrogen-ion concentration curve indicates that tungstic acid is not an ordinary dibasic acid —*vide infra*, sodium tungstate. W. Jander and A. Winkel found that the normal tungstate exists in soln. when the $[H^{\cdot}]$-concentration is between 10^{-14} and $10^{-6\cdot5}$; and the paratungstate when the $[H^{\cdot}]$-concentration is between $10^{-6\cdot5}$ and $10^{-1\cdot5}$. Meta- and para-tungstates are assumed to contain tungstic acid either in a polymerized form or in a semi-colloidal form. G. Jander also studied the tungstates from this point of view. W. V. Bhagwat and N. R. Dhar studied the ionization constants ; and S. Kato, the absorption spectra in the ultra-red, and the visible spectrum. L. Pissarjewsky found the heat of neutralization of tungstic acid, H_2WO_4, in 0·5N-NaOH, to be 13·698 Cals.

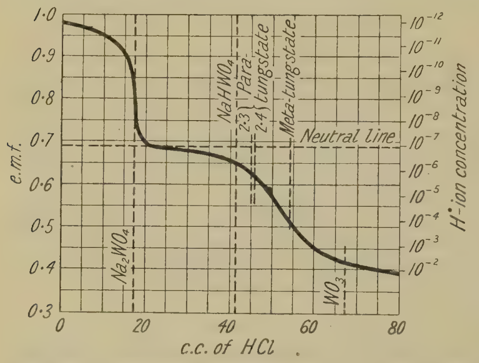


Fig. 24.—Electrometric Titration of Tungstic Acid.

A. Carnot [2] observed a hydrated form of tungsten trioxide associated with the scheelite of Meymac, Corrèze, France, and he accordingly called it **meymacite.** It is a yellow or greenish-yellow, friable earth sometimes having the general form of scheelite. Its composition approximates $WO_3.2H_2O$. G. C. Hoffmann also reported a pale yellow ochre associated with the scheelite of Marlow, Quebec, Canada.

According to T. Graham,[3] when dil. hydrochloric acid is added to a soln. of sodium tungstate until the liquid becomes slightly acid, a **colloidal solution of tungstic acid** is formed. A. P. Sabanéeff added that if the proportion of tungstate and acid is $2Na_2WO_4 : 3HCl$, and the mixture is dialyzed, the colloid is really sodium tungstate, $Na_2O.4WO_3$. T. Graham said that the colloid is tungstic acid from which all the sodium cannot be removed by dialysis. W. Biltz and A. von Vegesack said that the soln. remaining in the dialyzer contains $2Na_2O.11WO_3$, but considered that some colloidal tungstic acid is present. N. Pappada added that when moderately conc. hydrochloric acid is added drop by drop to a 5 per cent. soln. of sodium tungstate, a white gelatinous precipitate is formed when the liquids meet, but it quickly goes into soln., forming an acid liquor. The soln. contains colloidal tungstic acid, and he regards A. P. Sabanéeff's hypothesis, that it is $Na_2O.4WO_3$, as incorrect. According to A. Lottermoser, hydrochloric acid gives a voluminous, gelatinous, white precipitate with conc. soln. of sodium tungstate ; more dil. soln. remain clear at first, and afterwards slowly deposit the white precipitate in a more voluminous form. If the precipitate formed from the very dil. soln. is repeatedly decanted with distilled water, a clear hydrosol may be obtained, which, however, is unstable, as it gradually becomes cloudy, and changes to a hydrosol which is yellow in reflected light. When more conc. soln. are used, the voluminous, white precipitate gradually decreases in bulk, at the same time turning yellow ; finally, the same yellow hydrosol is obtained as previously. If this yellow hydrosol is shaken, a silky lustre is noticeable in reflected light, although it appears clear in transmitted light ; it is a suspension of relatively large particles, and gradually clears on keeping. L. Wöhler and W. Engels found that colloidal tungstic acid mixed with gelatin in the presence of ammonium chloride gives a flocculent precipitate which is peptized by an excess of ammonium chloride. W. A. Patrick mixed 3 to 8 per cent. soln. of a soluble salt, with vigorous stirring, with such a quantity of acid that the $H^{\cdot}$-ion conc. of the mixture is 0·1 to 0·5 mol per litre. The mixture is allowed to stand quietly for 2 to 5 hrs., until the soln. sets to a firm hydrogel. This is broken up, washed to remove salts and excess acid, and dried in a current of air at 75° to 120°, or heated to 300°–400° if a hard gel is desired. N. Pappada recommended preparing the colloid by the following process :

> Hydrochloric acid is added to a conc. soln. of sodium tungstate until the liquid has an acidic reaction. The white, gelatinous precipitate is washed several times by decantation at a low temp., 0° to 5°, while protecting the precipitate from currents of air which produce a change in the colloid. 15 parts of the tungstic acid are then dissolved by gently warming with a conc. soln. of one part of oxalic acid and the liquid dialyzed. If the outer water is frequently changed, the oxalic acid is completely removed, leaving a colloidal soln. of tungstic acid which may be concentrated in vacuo over sulphuric acid at ordinary temp. until it contains as much as 1·25 per cent. WO_3.

L. Moser and J. Ehrlich added hydrochloric acid of sp. gr. 1·19, drop by drop, to a soln. containing 32·89 grms. of normal sodium tungstate per litre. The precipitate at first formed was redissolved on continuing the addition of acid. The resulting soln. is colloidal, and can be coagulated by boiling. If nitric acid be used in place of hydrochloric acid, the precipitate does not redissolve with either cold or hot soln. The washed tungstic acid precipitated by hydrochloric acid, however, is partly soluble in hot nitric acid, while washed tungstic acid precipitated by nitric acid is no longer so easily soluble in hydrochloric acid. Sulphuric acid stands between hydrochloric and nitric acid in that the precipitate at first formed with this acid is partly redissolved on adding more acid. Consequently, although the tungstic acid precipitated by all the mineral acids is chemically the same, its physical condition depends on the nature of the acid. When the hydrochloric acid is added to the boiling soln. of sodium tungstate, at first a white precipitate forms which turns yellow, and passes into soln. with the exception of a few white particles which remain at the bottom of the vessel. If increasing amounts of acetic acid are added to the sodium tungstate soln., before adding the hydrochloric acid, the initial precipitation does not take place until greater amounts of hydrochloric acid are added, and this precipitate redissolves more quickly on adding more hydrochloric acid. However, the addition of 5 c.c. acetic acid to 2 c.c. of sodium tungstate soln. gives a precipitate which is not soluble in hydrochloric acid. If tungstic acid is precipitated from sodium tungstate soln. by hydrochloric acid and allowed to stand, the precipitate, at first white, becomes yellow and insoluble on adding more hydrochloric acid. If acetic acid is added, then hydrochloric acid, and the soln. heated, the precipitate again dissolves. The tungstic acid in all cases is positively charged. E. B. Miller and G. C. Connolly, and W. A. Patrick and E. H. Barclay prepared tungstic acid gels.

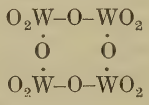
A. Müller prepared a colloidal soln. by dissolving 5 grms. of tungsten tetrachloride in 50 c.c. of a mixture of equal vols. of ethyl alcohol and ether, and the filtered soln. is then diluted to 250 c.c. with ethyl alcohol. If this soln. is mixed with an equal vol. of water, a colloidal soln. of tungstic acid is obtained, which can be kept for some days without any appreciable opalescence being observed. With larger quantities of water, coagulation takes place much more quickly. On adding small quantities of neutral salts or of hydroxides, coagulation occurs immediately; strong acids produce a similar effect after some minutes, but weak organic acids appear to exert no influence on the stability of the colloidal soln. A rise of temp. is also without influence, but coagulation takes place if the vol. is reduced to about a fourth of the original by evaporation. When an electric current is passed through the colloidal soln., a deep blue precipitate is formed at the cathode. This is attributed to reduction of the positively charged colloidal particles by the discharged hydrogen. The behaviour of the colloidal soln. towards electrolytes is consistent with the supposition that the tungstic acid is a positive colloid, and the spontaneous coagulation of the soln. is probably due to the presence of chlorine ions in the soln. According to M. Kröger the electrolysis of a 2 per cent. soln. of sodium tungstate between a mercury cathode and a silver anode produces the hydrosol of tungstic acid. The removal of alkali may be hastened by the cautious addition from time to time of a little hydrochloric acid, but in no circumstances may the neutral point be passed. Should the soln. become acid, blue tungsten compounds are produced. The tungsten hydroxide hydrosols are clear and transparent, but possess a deep brown colour, which in dil. soln. is yellowish-brown. They are coagulated by potassium chloride to form a black powder which resembles the lower oxides of tungsten. The coagulation of the colloid was studied by S. Ghosh and N. R. Dhar, A. Kargin, W. V. Bhagwat and N. R. Dhar, S. I. Diatschowsky, and K. Jacobsohn.

J. Duclaux said that colloidal soln. can be conc. by filtering out the solvent under press. through collodion. An increasing press. will remove more and more solvent, until a limit is attained where the colloid solidifies. This limiting press. is termed the " maximum osmotic pressure " of the colloid, and the limiting conc. the " solubility " of the colloid. In this sense, colloidal tungstic acid may be said to have a 60 per cent. solubility. N. Pappada prepared a soln. with 1·25 per cent. of WO_3, and it did not freeze at 0°. D. Klein said that when dried at 200°, the colloid has the composition $3WO_3.H_2O$. According to A. P. Sabanéeff, when colloidal tungstic acid is dried at 200°, it contains about 2·57 per cent. of H_2O and corresponds with $H_2W_3O_{10}$—mol. wt. 714; the mol. wt. calculated from the observed f.p. of the soln. is between 677 and 995. G. E. Linebarger measured the osmotic press. of soln. containing 0·02467 grm. and 0·0100 grm. of tungstic acid per c.c., and the values calculated for the mol. wt. of the colloidal tungstic acid averaged 1700, or nearly seven times 250, the number corresponding with the simple molecule H_2WO_4. The colloid mol. would therefore consist of seven simple mol. in the case of tungstic acid, and this is in keeping with the ordinary assumption that the mols. of colloids are very large. W. Biltz and A. von Vegesack made some observations on the osmotic press. A. V. Dumansky and co-workers discussed the formation of complexes as an intermediate stage in the formation of colloidal tungstic acid—*vide* colloidal molybdic acid. A. V. Dumansky and A. P. Buntin said that the electrical properties of the soln. indicate that the reaction takes place in stages: $Na_2WO_4+2HCl=H_2WO_4+2NaCl$ and $H_2WO_4+Na_2WO_4=Na_2O.2WO_3+H_2O$. This process is repeated, until a colloidal particle of the composition $Na_2O.nWO_3$, or $H_2[WO_4.nWO_3]$, is obtained. Numerous complexes of tungstic acid are known which confirm this view. They also measured the viscosity of tungstic acid sols. The hydrosol of tungstic acid, said T. Graham, has a bitter, astringent taste, and at 19°, the sp. gr. of a soln. with 5 per cent. WO_3 is 1·0475; with 10 per cent., 1·2168; 50 per cent., 1·6011; 66·5 per cent., 2·396; and 79·8 per cent., 3·243. C. E. Fawsitt found that the viscosity of the soln. is a linear function of the concentration: soln. with 2·8 and 4·4 per cent. of tungstic acid had viscosities 1·028 and 1·044 (water unity) respectively at 25°. N. R. Dhar and co-workers also measured the viscosity of the sol. S. Ghosh and N. R. Dhar measured the viscosity of the colloidal sol.; H. Pallman, and A. J. Rabinowitsch and V. A. Kargin, the $H^{\cdot}$-ion concentration of the hydrosol; and W. Riedal, the change in the electric conductivity with the age of the hydrosol.

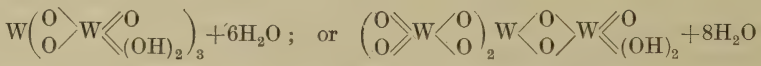
According to A. F. Wasiliewa-Sinzowa, when a colloidal soln. of tungstic acid in the presence of an organic reducing agent—*e.g.* dextrose, sucrose, dextrin, cellulose, or formaldehyde—is exposed to sunlight, it becomes blue. The soln. gradually loses this property at a speed which corresponds with a reaction of the first order. The reverse change occurs when the soln. is heated. It is assumed that colloidal tungstic acid exists in two modifications; the variety sensitive to the action of light is assumed to be converted into the other by the absorption of water; or the compound which is sensitive to light may be tungsten trioxide which on adsorbing a mol. of sodium tungstate forms the colloid which is not sensitive to light. According to A. F. Wasiliewa-Sinzova, when $0{\cdot}5N$-$Na_2WO_4.2H_2O$ is allowed to stand for t min. with an equal vol. of xN-HCl, and then mixed with 2 vols. of $0{\cdot}5N$-glucose, exposed for 5 min. to an arc-lamp, and the blue reduction product titrated with potassium permanganate, the latter result can be regarded as a measure of the sensitivity of the tungstic acid to light. The relation between the light sensitivity of the tungstic acid and the concentration, x, corresponded with the formula for a monomolecular reaction in which the constant k—using ordinary logarithms—decreased from 0·006 with $x=0{\cdot}43$ to 0·0003 with $x=0{\cdot}50$, and became constant when $x=0{\cdot}54$. The light sensitivity increases with x up to 0·47, then decreases—perhaps because the number of mols. of tungstic acid sensitive to light increases—and is then followed by a coagulating action of the acid. The decrease in the velocity constant with increasing values of x is attributed to the simultaneous decrease in the conc. of the WO_4''-ions which exert a catalytic effect. The conc. of this ion becomes zero when for every eq. of sodium tungstate an eq. of acid is present. The phenomena do not depend on the Cl'-ions of the acid because similar results are obtained with sulphuric acid. L. Wöhler and W. Engels showed that the precipitation which occurs when soln. of molybdates are acidified is due to the presence of tungstates. The readiness with which precipitation takes place is dependent on the proportion of tungstic acid present, and when this is present in very small amount, the temp. may be raised to nearly 100° before a precipitate is obtained. The precipitation is primarily due to the tungstic acid in the soln., and when this separates out, molybdic acid is simultaneously removed from the soln. S. Glixelli studied the electroösmosis or cataphoresis. T. Graham found that the gelatilization of silicic acid is retarded by the presence of colloidal tungstic acid; M. Kröger measured the time required for the complete gelatinization of silicic acid with different conc. of tungstic acid and found that the time-conc. curve passes first through a minimum with the addition of tungstic acid soln., it then passes through a maximum, and finally falls continuously with increasing proportions of tungstic acid. E. Wedekind and H. Fischer said that hydrated tungstic acid does not adsorb prussian blue. The stability of the colloid was studied by S. I. Diatschowsky. The adsorption of water, ethyl alcohol, ethylacetate, and acetic acid vapours was studied by J. N. Pearce and M. J. Rice.

F. Margueritte[4] obtained the ammonium salt of an acid which A. Laurent called **metatungstic acid ;** the former represented it by $(NH_4)_2O.3WO_3.5H_2O$, and the latter by $5(NH_4)_2O.18WO_3.31H_2O$. W. Lotz showed that the ratio of base to acid, $R_2O : WO_3$ is more nearly 1 : 4, and this is in accord with the observations of A. Riche, W. Lotz, R. Scheibler, and J. C. G. de Marignac on these salts. The corresponding acid was obtained by A. Laurent by treating a soln. of the ammonium salt with hydrochloroplatinic acid, filtering off the ammonium chloroplatinate, and evaporating the filtrate for crystallization. The colourless crystals of the metatungstic acid, $H_2O.4WO_3.9H_2O$, are readily soluble in water and alcohol. C. Scheibler treated the barium salt with the calculated amount of dil. sulphuric acid, and evaporated the filtrate over sulphuric acid in vacuo. A similar process was employed by E. Péchard, and M. Soboleff. V. Forcher treated the lead salt with hydrogen sulphide, expelled the excess of that gas by a current of carbon dioxide, concentrated the soln. on a water-bath, and finished the evaporation for crystallization over sulphuric acid, in vacuo. J. Lefort treated a conc. soln. of sodium ditungstate with arsenic acid and warmed the mixture. A. Rosenheim and F. Kohn obtained metatungstic acid by treating a conc. aq. soln. of ammonium metatungstate with ether and conc. hydrochloric or sulphuric acid. Three layers of liquid are formed; the lower layer contains free metatungstic acid, together with ether and the mineral acids. The required acid is obtained by evaporating this layer in air. The soluble tungstic acid described by J. Persoz was probably metatungstic acid.

Analyses by M. Soboleff, etc. agree with the formula $H_2W_4O_{13}.8H_2O$, or $H_2W_4O_{13}.6H_2O$. A. Rosenheim and F. Kohn gave $H_2W_4O_{13}.8H_2O$ and $H_2W_4O_{13}.6H_2O$. According to D. I. Mendeléeff, the same transformation is accomplished in the passage of ordinary tungstates into the metatungstates as takes place in the passage of tungstic acid itself from an insoluble into a soluble state—the hydrosol. A. Michaelis represented ordinary tungstic acid by H_2WO_4, and he regarded metatungstic acid as a condensation product of this acid, $H_2W_4O_{13}.nH_2O$, derived from the anhydride, W_4O_{12}, or, with tungsten sexivalent,



The question is not so easily decided. The complex heteropoly-acids of tungsten have been discussed by A. Rosenheim and co-workers, as well as by W. Prandtl and co-workers, A. Rogers and E. F. Smith, P. Pfeiffer, H. Copaux, etc. C. Scheibler showed that all the metatungstates are dehydrated with difficulty, and that after all the water has been expelled, the residue no longer dissolves in water. This makes it probable that part at least of the water is constitutional. A. Geuther represented metatungstic acid by formulæ which assumed that all the tungsten atoms are sexivalent, and that one mol. or three mols. of water are constitutional:



$$W\Big(\begin{smallmatrix}O\\O\end{smallmatrix}\!>\!W\!\ll\!\begin{smallmatrix}O\\(OH)_2\end{smallmatrix}\Big)_3+6H_2O\,; \quad \text{or} \quad \Big(\begin{smallmatrix}O\\O\end{smallmatrix}\!\gg\!W\!<\!\begin{smallmatrix}O\\O\end{smallmatrix}\Big)_2W\!<\!\begin{smallmatrix}O\\O\end{smallmatrix}\!>\!W\!\ll\!\begin{smallmatrix}O\\(OH)_2\end{smallmatrix}+8H_2O$$

C. Friedheim found that the ammonium and potassium salts lose all but one mol. of water at 100°, whilst the sodium, barium, cadmium, lead and manganese salts retain 3 mols. at 100°, and, with the exception of the lead salt, they retain one mol. up to 220°. This makes it appear as if at least one and possibly 3 mols. of water are constitutional. H. Copaux argued that metatungstic acid is isomorphous with the complex heteropoly acids—*e.g.* boro-, phosphato-, and silico-tungstic acids—and that some of the salts—those of ammonium, potassium, and barium—are also isomorphous, and consequently, these compounds have probably a similar constitution; and if the mol. wt. be increased six times, the potassium salts can be represented: $6K_2O.(3H_2O.24WO_3).36H_2O$, $5K_2O.(B_2O_3.24WO_3).36H_2O$, and $4K_2O.(2SiO_2.24WO_3).36H_2O$; and the barium salts: $6BaO(3H_2O.24WO_3).54H_2O$, and $5BaO(B_2O_3.24WO_3).54H_2O$. The mol. proportion of acid and base is not the same in the isomorphous compounds, but if 3 mols. of water are assumed to be constitutional in metatungstic acid, the proportions of water of crystallization are the same. There are also several points of resemblance in the properties of the salts of these heteropolyacids. It is therefore assumed that the 3 mols. of constitutional water are acidic, and the free acids can be represented by the formulæ: $6H_2O(3H_2O.24WO_3).48H_2O$; $5H_2O.(B_2O_3.24WO_3).48H_2O$; $4H_2O.(2SiO_2.24WO_3).48H_2O$; and $3H_2O.(P_2O_5.24WO_3).48H_2O$.

A. Rosenheim and F. Kohn tried to find how much water is constitutional by preparing insoluble salts which usually do not contain water of crystallization, and showed that in the silver salt 2 or 3 mols. are firmly combined with the molecule, while in the thallium and guanidinium salts, only one mol. is firmly combined. They also showed that the ratio of fixed water to the WO_3 group is at least 1 : 4 and probably 3 : 4, whereas H. Copaux's hypothesis requires this ratio to be 1 : 8. A. Rosenheim and F. Kohn concluded that the constitution is best represented by a formula of the co-ordination type with 3 mols. of constitutional water: $R_2[WO(WO_4)_3(H_2O)_3]$, or possibly $R_2[WO(WO_4)_3(H_2O)]$. When the constitutional water is expelled, the salts are decomposed. H. Copaux then modified this hypothesis, and represented the salts as derivatives of the acid (hypothetical):

Metatungstic acid	$H_{10}[H_2(W_2O_7)_6]$
Borotungstic acid	$H_9[B(W_2O_7)_6]$
Silicotungstic acid	$H_8[Si(W_2O_7)_6]$
Phosphotungstic acid	$H_7[P(W_2O_7)_6]$

where the basicity is determined by the difference between the valency of the central element and the combined valency of associated six radicles. Metatungstic acid can thus be referred to water $H_{10}[H_2O_6]$ in which the six oxygen atoms are replaced by six bivalent W_2O_7-radicles. The acid is thus assumed to be decabasic, whereas, with the exception of the mercury salt, only hexabasic salts of the type $M_6H_4[H_2(W_2O_7)_6]$ have been prepared. An ill-defined mercurous salt, $Hg^{\cdot}{}_8H_2[H_2(W_2O_7)_6]$, has been reported—*vide infra*. Actually the basicity of the acid is unknown.

The crystals of metatungstic acid were described by V. Forcher as octahedra, while C. Scheibler called them tetragonal bipyramids. H. Copaux found that the crystals are isomorphous with those of the silico- and phospho-tungstic acids. C. Scheibler found that the sp. gr. is 3·93. The sp. gr. of the aq. soln. with 41·46, 88·57, and 111·87 grms. of $H_2W_4O_{13}.9H_2O$ were found by M. Soboleff to be respectively 1·6025 at 0°; 2·5239 at 22°; and 3·6503 at 43·5°; and he gave for soln. with p per cent. of WO_3 at 17·5°, the sp. gr. $=1+0{\cdot}00903p+0{\cdot}0000633p^2+0{\cdot}00000141p^3$. The crystals, said A. Rosenheim and F. Kohn, readily effloresce in air. M. Soboleff added that when heated to 50°, the crystals lose 8·34 per cent. or $4{\cdot}5H_2O$, and they then become virtually insoluble in water, this means that the acid is decomposed. The loss at 100° is 10·1 per cent. or $6{\cdot}1H_2O$; at 150°, 12·94 per cent. or $7{\cdot}5H_2O$; at 180°, 13·5 per cent. or $8{\cdot}1\ H_2O$, and at 180°, 13·48 or $8H_2O$. C. Scheibler gave 11·4 per cent. or $7H_2O$ for the loss at 100°. According to M. Soboleff, the lowering of the f.p. of soln. of the acid with 0·3489, 2·8724, and 25·9447 grms. of $H_2W_4O_{13}$ per 100 c.c. of water are respectively 0·05165°, 0·04076°, and 0·03393°, corresponding with the respective mol. wts. 365·2, 464·7, and 557·9—theory 926—so that the factors i are respectively 2·53, 1·99, and 1·66. The mol. electrical conductivities, μ, of the aq. soln. with 926 grms. in v litres, at 25°, are:

v .	32	64	128	256	512	1024
μ .	159·9	219·1	261·8	305·1	348·6	390·9

A. Rosenheim and F. Kohn said that in aq. soln., metatungstic acid behaves as a normal electrolyte, and acts as a dibasic acid. For the electrometric titration, *vide supra*, Fig. 24. The solubilities of $H_2W_4O_{13}.9H_2O$ at 0°, 22°, and 43·5° are respectively 41·46, 88·57, and 111·87 grms. per 100 c.c. of water. The aq. soln. is colourless, or, according to V. Forcher, pale yellow. The soln. has a strong acid and bitter taste, and does not appear to be poisonous. A. Rosenheim and E. Brauer found the $H^{\cdot}$-ion conc. of 0·005N-soln. of $H_{10}[H_2(W_2O_7)_6].22H_2O$, to be $[H^{\cdot}]=0{\cdot}0035$, or $p_H=2{\cdot}45$, when the values for 0·01N-HCl are $[H^{\cdot}]=0{\cdot}0095$, or $p_H=2{\cdot}022$; and for N-$CH_3.COOH$, $[H^{\cdot}]=0{\cdot}0043$, or $p_H=2{\cdot}366$. H. Leiser found that while no change occurred in the electrolysis of a tungstate, a soln. of metatungstic acid is reduced to a blue soln. which is readily oxidized by exposure to air, and from which no crystalline product could be obtained. Using a platinum basin as cathode, and a nickel gauze anode, the blue compound formed approximates W_4O_{11}, and if a lead cathode be employed the reduction goes further forming black tungsten dioxide. According to C. Scheibler, the aq. soln. can be boiled for a long time without decomposition, and at 100°, the soln. can be evaporated to a certain point when it forms a white gummy mass of white tungstic acid which suddenly cracks, and finally yellow tungstic acid is formed. Dil. soln. can be kept for a long time in closed vessels without change, but conc. soln. slowly form white tungstic acid. If the soln. is not too dil., sulphuric acid gives a white precipitate which passes into soln. if more water is added. V. Forcher, and C. Scheibler added that with hydrochloric acid and zinc, metatungstic acid becomes blue; the soln. gives no precipitate with hydrogen sulphide; and with ammonium sulphide, sulphur separates out, and after a time, the soln. deposits bluish-black cubes of ammonium sulphotungstate. J. C. Ghosh and J. Mukherjee studied tungstic acid as a photocatalyst in the decomposition of hydrogen dioxide. A. Rosenheim and F. Kohn said that in alcoholic soln., metatungstic acid acts as a colloid; when a mineral acid is present, it is possible that a mol. compound of metatungstic acid and ether is formed. No esters of metatungstic acid could be prepared. M. Soboleff said that at 0°, 7·8°, 18·2° and 24·2°, ether dissolves respectively 83·456, 88·389, 99·66, and 110·76 grms. $H_2W_4O_{13}.9H_2O$ per 100 c.c. If the acid has lost some water it does not dissolve. In extracting the acid from aq. soln. by means of ether, a liquid with 3 layers is formed. G. Jander and co-workers regard the metatungstates as hexatungstates, possibly $R_6H_4[H_2(W_2O_7)_6].nH_2O$. They found that when aq. soln. of alkali tungstates are gradually acidified, amorphous precipitates of hydrated forms of tungsten trioxide are finally obtained. Before the precipitate is actually formed, however, polymerization changes occur in the dissolved tungstic acid, and these changes have been investigated by the two methods already used in the case of stannates, *viz.*, by means of measurements of diffusion coefficients and of absorption coefficients of visible and ultra-violet light. The gradual addition of hydrochloric acid to a soln. of an alkali tungstate produces first a polymerization to hexatungstic acid, without the formation of any intermediate acid, as follows: $6WO_4''+6H^{\cdot}\rightleftharpoons W_6O_{21}''''''+3H_2O$. With the addition of more acid there is a further polymerization to metatungstic acid, which is probably a diparatungstic acid, and in presence of other acids, such as arsenic or phosphoric acids, heteropolytungstic acids are formed.

According to J. Lefort, if a very conc., cold soln. of one part of arsenic acid is mixed with a similar soln. of four parts of normal sodium tungstate, a complex arsenatotungstate is formed, but if one part of arsenic acid be mixed with two parts of sodium ditungstate, and the soln. evaporated, metatungstic acid is obtained in very fine yellow leaflets. To this acid, the name **metaluteotungstic acid,** $WO_3.7H_2O$, is given—luteus, yellow. This acid is also obtained if phosphoric acid is used instead of arsenic acid. The properties resemble those of ordinary metatungstic acid. The yellow colour may be due to impurities; E. Péchard could not confirm J. Lefort's results.

In 1847, A. Laurent[5] prepared salts of a **paratungstic acid.** He called them paratungstates, and represented them by the formula $5R_2O.12WO_3$, while W. Lotz, and C. Scheibler suggested $3R_2O.7WO_3$. J. C. G. de Marignac concluded that the majority of the paratungstates contained $5R_2O.12WO_3$, but a few contained $3R_2O.7WO_3$. G. von Knorre, and C. Gonzalez were unable to decide in favour of either formula. The degree of purity of the salts, and the limits of the analytical errors do not enable a distinction to be made between these formulæ. H. Copaux studied the dehydration of the salts, and concluded that they are hydrohexatungstates with the general formula $R_5[H(W_2O_7)_3].nH_2O$. He preferred this to a formula with the WO''_4-radicle because like the metatungstates the paratungstates absorb ultra-violet light, whereas the normal tungstates do not do so. A. Rosenheim regarded the paratungstates as salts of the acid $H_{10}[H_2(WO_4)_6]$. There is no evidence proving the basicity of the acid, but the salts are usually representable by the formula $R_5H_5[H_2(WO_4)_6]$. G. von Knorre found that the paratungstates gradually decompose in aq. soln., forming normal tungstates and metatungstates; hence, while a freshly prepared soln. is neutral to phenolphthalein, it gradually becomes acidic. The change proceeds rapidly when the soln. is boiled. R. C. Wells also found that the electrical conductivities of aq. soln. slowly increase when allowed to stand for some time.

L. A. Hallopeau found that free paratungstic acid is not easily obtained by the action of hydrogen sulphide on the lead salt, or of hydrochloric acid on the silver salt, because the resulting silver chloride is difficult to separate. The best method is to mix the barium salt with not quite enough dil. sulphuric acid for the complete decomposition of the salt. Dil. soln. of paratungstic acid are not decomposed by heat, but prolonged boiling partially converts the paratungstic into metatungstic acid. When the soln. is evaporated, even in vacuo, at the ordinary temp., some ordinary tungstic acid is formed. Alkali-lye neutralizes the soln. and yields paratungstates. Hydrochloric, nitric, and sulphuric acids decompose dil. soln. of paratungstic acid; hydrogen sulphide reduces them with formation of the blue or the green oxide; acetic, phosphoric, and carbonic acids have no action. Organic substances, including filter-paper, reduce the acid with formation of the blue oxide, and a soln. mixed with alcohol is similarly reduced when exposed to light. For the electrometric titration, *vide supra*, Fig. 24.

REFERENCES.

[1] E. Zettnow, *Pogg. Ann.*, **130**. 46, 1867; J. J. and F. de Elhuyar, *Análisis quimico de volfram y exámen de un nuovo metal que entra en su composicion*, Bascongada, 1783; *A Chemical Examination of Wolfram and Examination of a New Metal which enters into its Composition*, London, 1785; *Chemische Zerkliederung des Wolframs*, Halle, 1786; *Mém. Acad. Toulouse*, **2**. 141, 1784; C. D. Braun, *Journ. prakt. Chem.*, (1), **91**. 39, 1864; E. F. Anthon, *ib.*, (1), **9**. 6, 1836; V. Forcher, *ib.*, (1), **86**. 227, 1862; *Bull. Soc. Chim.*, (2), **5**. 197, 1863; *Sitzber. Akad. Wien*, **44**. 165, 1861; H. T. S. Britton, *Journ. Chem. Soc.*, 147, 1927; H. T. S. Britton and W. L. German, *ib.*, 1249, 1930; A. Laurent, *Compt. Rend.*, **25**. 538, 1847; *Ann. Chim. Phys.*, (3), **21**. 62, 1847; A. Riche, *Recherches sur le tungstène et ses composés*, Paris, 1857; (3), **50**. 15, 1857; J. C. G. de Marignac, *ib.*, (3), **69**. 14, 1863; C. W. Scheele, *Akad. Handl. Stockholm*, **2**. 89, 1781; *Journ. Phys.*, **22**. 724, 1783; H. E. Roscoe, *Liebig's Ann.*, **162**. 359, 1872; *Proc. Manchester Lit. Phil. Soc.*, **11**. 79, 1872; *Chem. News*, **25**. 61, 73, 90, 1873; *Bull. Soc. Chim.*, (2), **25**. 61, 1873; J. J. Berzelius, *Schweigger's Journ.*, **16**. 476, 1816; *Ann. Phil.*, **3**. 245, 1814; *Ann. Chim. Phys.*, (2), **17**. 13, 1821; *Pogg. Ann.*, **4**. 147, 1825; **8**. 147, 267, 1826; L. Pissarjewsky, *Zeit. anorg. Chem.*, **24**. 115, 1900; G. F. Hüttig and B. Kurre, *ib.*, **122**. 44, 1922; **126**. 170, 1922; G. F. Hüttig, *Zeit. angew. Chem.*, **35**. 391, 1922; *Koll. Zeit.*, **35**. 337, 1924; H. C. Burger, *Zeit. anorg. Chem.*, **121**. 240, 1922; J. A. M. van Liempt, *ib.*, **127**. 215, 1923; H. Schmidt, *Amer. Chem. Journ.*, **8**. 16, 1886; J. W. Mallet, *Journ. Chem. Soc.*, **28**. 1228, 1875; R. C. Wells, *Journ. Amer. Chem. Soc.*, **29**. 112, 1907; S. C. Lind and B. C. Trueblood, *ib.*, **29**. 477, 1907; R. F. Bernhardi-Grisson, *Die kathodische Reduktion der Wolframsaure*, Berlin, 1910; A. Rosenheim and R. F. Bernhardi-Grisson, *Proc. Internat. Congress, Appl. Chem.*, **7**. x, 120, 1911; A. Pinagel, *Beiträge zur Kenntnis der Wolframate und Silicowolframate*, Bern, 10, 1904; B. Kellner, *Untersuchungen über Perwolframate*, Berlin, 1909; J. Eltzbacher, *Beiträge zur Elektrochemie der Wolframate*, Berlin, 10, 1899; F. Hundeshagen, *Chem. Ztg.*, **18**. 547, 1894; O. Hertig, *Zeit. angew. Chem.*, **14**. 165, 1901; M. E. Chevreul, *Ann. Phil.*, **12**. 144, 1818; *Bull. Philomath.*, 20, 1818; G. Jander, *Zeit. angew. Chem.*, **41**. 201, 1928; D. Mojert, *Die Vorgänge in wässerigen Lösungen von Wolframaten bei Veränderung der Wasserstoffionenkonzentration*, Göttingen, 1929; D. D. Pierce and L. F. Yntema, *Journ. Phys. Chem.*, **36**. 1822, 1930; A. Rosenheim and A. Wolff, *Zeit. anorg. Chem.*, **193**. 47, 64, 1930; A. Wolff, *Zur Kenntnis der Parawolframate und einiger Hetropolywolframate*, Berlin, 1930; A. M. Morely, *Journ. Chem. Soc.*, 1987, 1930; W. V. Bhagwat and H. R. Dhar,

Journ. Indian Chem. Soc., **6**. 807, 1929; G. Jander and W. Heukeshoven, *Zeit. anorg. Chem.*, **187**. 60, 1930; G. Jander and T. Aden, *Zeit. phys. Chem.*, **143**. 197, 1930; S. Kato, *Science Papers Tokyo Inst. Phys. Chem. Research*, **13**. 7, 49, 1930; A. Dyachkovsky, *Journ. Russ. Phys. Chem. Soc.*, **61**. 423, 1929; M. L. Holt and L. Kahlenberg, *Trans. Amer. Electrochem. Soc.*, **57**. 361, 1930; A. Lottermoser, W. Riedel and O. Bretschneider, *Zeit. Elektrochem.*, **36**. 183, 1930; W. Jander and A. Winkel, *Zeit. phys. Chem.*, **149**. 97, 1930.

[2] A. Carnot, *Compt. Rend.*, **79**. 638, 1874; G. C. Hoffmann, *Ann. Rep. Geol. Sur. Canada*, **7**. 14, 1896.

[3] T. Graham, *Journ. Chem. Soc.*, **17**. 318, 1864; *Proc. Roy. Soc.*, **13**. 340, 1864; *Phil. Mag.*, (4), **28**. 314, 1864; *Pharm. Journ.*, (2), **6**. 63, 1865; *Liebig's Ann.*, **135**. 65, 1865; *Journ. prakt. Chem.*, (1), **94**. 347, 1865; *Bull. Soc. Chim.*, (2), **2**. 185, 1864; *Ann. Chim. Phys.*, (4), **3**. 128, 1864; *Compt. Rend.*, **59**. 174, 1864; J. Duclaux, *ib.*, **148**. 295, 1909; N. Pappada, *Gazz. Chim. Ital.*, **32**. ii, 22, 1902; W. A. Patrick, *Brit. Pat. No.* 136543, 1919; 212065, 1923; *U.S.A. Pat. No.* 1682239, 1928; W. A. Patrick and E. H. Barclay, *ib.*, 1683695, 1928; E. B. Miller and G. C. Connolly, *ib.*, 289890, 1928; D. Klein, *Bull. Soc. Chim.*, (2), **36**. 643, 1881; L. Moser and J. Ehrlich, *Edel-Erden Erze*, **3**. 40, 65, 1922; S. I. Diatschowsky, *Journ. Russ. Phys. Chem. Soc.*, **61**. 423, 1929; A. P. Sabanéeff, *ib.*, **21**. 515, 1889; **22**. 102, 1890; *Zeit. anorg. Chem.*, **14**. 354, 1897; S. Glixelli, *Anz. Akad. Wien*, **54**. 102, 1917; C. E. Linebarger, *Amer. Journ. Science*, (3), **43**. 218, 1892; A. Lottermoser and W. Riedel, *Koll. Zeit.*, **52**. 133, 1930; W. Riedel, *Untersuchungen an Wolfram- und Chromhydrosolen*, Dresden, 1930; A. Lottermoser, *Verh. Ges. deut. Naturforsch. Aerzte*, ii, 70, 1910; *Bemmelen's Festschrift*, 152, 1911; A. Müller, *ib.*, 416, 1911; *Koll. Zeit.*, **8**. 93, 1911; M. Kröger, *ib.*, **30**. 16, 18, 1922; N. R. Dhar and N. D. and M. N. Chakravarti, *ib.*, **44**. 225, 1928; L. Wöhler and W. Engels, *Koll. Beihefte*, **1**. 454, 1910; *Zeit. Elektrochem.*, **16**. 693, 1910; A. F. Wasiliewa, *Chem. Ztg.*, **36**. 199, 1912; *Journ. Russ. Phys. Chem. Soc.*, **44**. 819, 1912; *Zeit. wiss. Photochem.*, **12**. 1, 1913; A. F. Wasiliewa-Sinzova, *Journ. Chim. Ukraine*, **1**. 425, 1925; W. Biltz and A. von Vegesack, *Wallach's Festschrift*, 152, 1910; *Zeit. phys. Chem.*, **68**. 357, 1909; W. Biltz, *Ber.*, **37**. 1095, 1766, 1904; C. E. Fawsitt, *Journ. Chem. Soc.*, **93**. 1004, 1908; A. V. Dumansky, A. P. Buntin, S. I. Diatschowsky and A. G. Kniga, *Koll. Zeit.*, **38**. 208, 1926; *Journ. Russ. Phys. Chem. Soc.*, **58**. 326, 1926; A. V. Dumansky and A. P. Buntin, *ib.*, **58**. 107, 1926; E. Wedekind and H. Fischer, *Ber.*, **60**. B, 544, 1927; J. N. Pearce and M. J. Rice, *Journ. Phys. Chem.*, **33**. 692, 1929; S. Ghosh and N. R. Dhar, *ib.*, **33**. 1905, 1929; *Zeit. anorg. Chem.*, **190**. 421, 1930; *Journ. Phys. Chem.*, **33**. 1905, 1929; W. V. Bhagwat and N. R. Dhar, *Journ. Indian Chem. Soc.*, **6**. 781, 807, 1929; A. Rabinowitsch and V. A. Kargin, *Zeit. phys. Chem.*, **152**. 24, 1931; V. Kargin, *Koll. Zeit.*, **49**. 281, 1929; H. Pallman, *Koll. Beihefte*, **30**. 334, 1930; K. Jacobsohn, *Ueber Taktosole*, Dresden, 1929.

[4] A. Michaelis, *Ausführliches Lehrbuch der Chemie*, Braunschweig, **2**. 1153, 1881; A. Geuther, *Lehrbuch der Chemie*, Jena, 624, 1870; C. Friedheim, *Ueber die Konstitution der Metawolframsäure und ihrer Salze*, Freiburg i. B., 1882; D. I. Mendeléeff, *The Principles of Chemistry*, London, **2**. 282, 1891; St. Petersburg, 666, 1903; C. Scheibler, *Bull. Soc. Chim.*, (2), **4**. 256, 1862; *Chem. News*, **6**. 181, 1862; *Journ. prakt. Chem.*, (1), **80**. 204, 1860; (1), **83**. 273, 1861; V. Forcher, *ib.*, (1), **86**. 227, 1862; *Bull. Soc. Chim.*, (2), **5**. 197, 1863; *Sitzber. Akad. Wien*, **44**. 165, 1861; A. Laurent, *Compt. Rend.*, **25**. 538, 1847; *Ann. Chim. Phys.*, (3), **21**. 62, 1847; E. Péchard, *ib.*, (6), **22**. 198, 1891; A. Riche, *ib.*, (3), **50**. 5, 1857; J. Lefort, *ib.*, (5), **25**. 200, 1882; *Journ. Pharm. Chim.*, (4), **4**. 221, 1881; *Compt. Rend.*, **92**. 1461, 1881; F. Margueritte, *ib.*, **17**. 742, 1843; **20**. 294, 1845; *Journ. Pharm. Chim.*, (3), **4**. 383, 1843; (3), **7**. 222, 1845; (3), **10**. 442, 1846; *Ann. Chim. Phys.*, (3), **17**. 475, 1846; J. C. G. de Marignac, *ib.*, (3), **69**. 5, 1863; *Compt. Rend.*, **55**. 888, 1862; J. Persoz, *Ann. Chim. Phys.*, (4), **1**. 93, 1864; *Compt. Rend.*, **34**. 135, 1852; H. Copaux, *ib.*, **147**. 973, 1908; **148**. 633, 1909; *Ann. Chim. Phys.*, (8), **17**. 217, 1909; *Zeit. anorg. Chem.*, **70**. 297, 1911; **74**. 351, 1912; M. Soboleff, *ib.*, **12**. 16, 1896; A. Rosenheim and F. Kohn, *ib.*, **69**. 247, 1911; A. Rosenheim, in R. Abegg, *Handbuch der anorganischen Chemie*, Leipzig, **4**. i (2), 977, 1921; *Zeit. anorg. Chem.*, **70**. 418, 1911; **75**. 141, 1912; **93**. 273, 1915; A. Rosenheim and J. Jänicke, *ib.*, **77**. 239, 1912; E. Rosenheim and E. Brauer, *ib.*, **93**. 284, 1915; A. Rosenheim and H. Schwer, *ib.*, **89**. 224, 1914; A. Rosenheim, M. Pieck and J. Pinsker, *ib.*, **96**. 139, 1916; W. Prandtl, *Ber.*, **48**. 692, 1915; W. Prandtl and H. Hecht, *Zeit. anorg. Chem.*, **92**. 198, 1915; P. Pfeiffer, *ib.*, **105**. 26, 1919; G. Jander, D. Mojert and T. Aden, *ib.*, **180**. 129, 1929; G. Jander and T. Aden, *Zeit. phys. Chem.*, **144**. 197, 1929; W. Lotz, *Liebig's Ann.*, **91**. 52, 1854; *Journ. prakt. Chem.*, (1), **63**. 209, 1854; *Ann. Chim. Phys.*, (3), **43**. 246, 1855; J. C. Ghosh and J. Mukherjee, *Journ. Indian Chem. Soc.*, **6**. 231, 1929; G. Wyrouboff, *Bull. Soc. Min.*, **15**. 65, 1892; A. Rogers and E. F. Smith, *Journ. Amer. Chem. Soc.*, **26**. 1474, 1904; H. Leiser, *Zeit. Elektrochem.*, **13**. 690, 1907.

[5] A. Laurent, *Compt. Rend.*, **25**. 538, 1847; *Ann. Chim. Phys.*, (3), **21**. 62, 1847; W. Lotz, *ib.*, (3), **43**. 246, 1855; *Liebig's Ann.*, **91**. 52, 1854; *Journ. prakt. Chem.*, (1), **63**. 209, 1854; C. Gonzalez, *ib.*, (2), **36**. 44, 1887; C. Scheibler, *ib.*, (1), **80**. 204, 1860; (1), **83**. 273, 1861; *Chem. News*, **6**. 181, 1862; *Bull. Soc. Chim.*, (2), **4**. 256, 1862; G. von Knorre, *Ber.*, **18**. 2362, 1885; **19**. 819, 1886; R. C. Wells, *Journ. Amer. Chem. Soc.*, **29**. 112, 1907; J. C. G. de Marignac, *Ann. Chim. Phys.*, (3), **69**. 5, 1863; *Compt. Rend.*, **55**. 888, 1862; L. A. Hallopeau, *ib.*, **121**. 61, 1895; *Ann. Chim. Phys.*, (7), **19**. 135, 1900; H. Copaux, (8), **17**. 217, 1909; *Compt. Rend.*, **156**. 1771, 1913; *Zeit. anorg. Chem.*, **70**. 297, 1911; **74**. 351, 1912; A. Rosenheim, *ib.*, **93**. 273, 1915; **96**. 139, 1916.

§ 12. The Monotungstates—Normal Tungstates

The great variety of compounds of tungsten trioxide with the bases has introduced difficulties in their classification. Some consider that they are best regarded as normal tungstates of the type, $M_2WO_4.nH_2O$; paratungstates of the type $3M_2O.7WO_3.nH_2O$, or $5M_2O.12WO_3.nH_2O$; and metatungstates of the type $M_2W_4O_{13}.nH_2O$; there are, however, other relations which make this system inadequate—*vide supra,* tungstic acid. As in the case of the higher molybdates (*q.v.*), many of the complex tungstates can be regarded as

Hexa-tungstates	Ditungstates or Tetrahydrohexatungstates . . .	$R_6H_4[H_2(WO_4)_6]$
	Paratungstates or Pentahydrotungstates . . .	$R_5H_5[H_2(WO_4)_6]$
	Tritungstates or Hexahydrohexatungstates . . .	$R_4H_6[H_2(WO_4)_6]$
Dodeca-tungstates	Metatungstates or Tetrahydrododecatungstates . .	$R_6H_4[H_2(W_2O_7)_6]$
	Hexatungstates or Hexahydrododecatungstates . .	$R_4H_6[H_2(W_2O_7)_6]$
	Octotungstates or Heptahydrododecatungstates . .	$R_3H_7[H_2(W_2O_7)_6]$

Hydrated tungsten trioxide readily dissolves in aq. ammonia, but neither E. F. Anthon,[1] nor J. C. G. de Marignac were able to isolate normal **ammonium tungstate,** $(NH_4)_2WO_4.nH_2O$, from the soln. because when the soln. is concentrated, ammonia is lost, and an acid salt remains. The corresponding sulpho-salt, $(NH_4)_2WS_4$, has been obtained. It is assumed that an aq. soln. of the salt exists because, as shown by E. F. Anthon, a soln. of calcium chloride precipitates normal calcium tungstate. A. Rosenheim and F. Jacobsohn, however, did obtain the normal salt as a white mass by the action of hydrated tungstic acid on liquid ammonia. Likewise the salt was prepared by T. H. Tsao, and by E. Kunau. For the so-called *ammonium isotungstate, vide supra,* the history of tungsten. Ammonium tungstate is very soluble in water, and readily loses ammonia. According to C. E. Guignet, the aq. soln. readily dissolves prussian blue; and, according to R. E. Liesegang, paper treated first with ammonium tungstate, and then with hydrochloric acid, becomes grey when exposed to light. According to K. A. Hofmann and V. Kohlschütter, when 25 grms. of powdered sodium paratungstate are added to a soln. of 10 grms. of hydroxylamine hydrochloride in 20 c.c. of water, the product dissolved in 50 c.c. of 15 per cent. ammonia, and the soln. allowed to evaporate over potassium hydroxide, thick tablets of **ammonium hydroxylamine tungstate,** $(NH_3OH).WO_4.(NH_4)$, are formed. The salt reduces Fehling's soln., and an ammoniacal soln. of silver nitrate.

G. C. Gmelin[2] obtained **lithium tungstate,** Li_2WO_4, by dissolving tungsten trioxide in a boiling soln. of lithium carbonate, and evaporating the liquid for crystallization; and E. F. Anthon obtained it by dissolving the tungsten trioxide in molten lithium carbonate, and allowing an aq. soln. of the cold product to crystallize. J. A. M. van Liempt found that lithium tungstate melts at 742° and shows no transition point. F. Hoermann gave 742° for the m.p. The f.p. of mixtures with tungsten trioxide are shown in Fig. 25, as far as about $Li_2O : WO_3 = 1 : 2{\cdot}5$; the molten tungstate does not dissolve more trioxide. A compound lithium ditungstate is formed melting at 745°, and with a transition point at 687°. The curve Fig. 25 is by F. Hoermann. *Vide infra,* for mixtures of lithium tungstate with sodium and potassium tungstates. According to W. Zachariasen, the X-radiogram shows that lithium tungstate is isomorphous with the molybdate (*q.v.*); the elementary trigonal cell has *a* about 8·20 A., and *c*, about 9·45 A. The rhombic columns, or octahedral crystals, are stable in air; they have a sweet, yet bitter, taste; they are readily soluble in water; and the aq. soln. has an alkaline reaction.

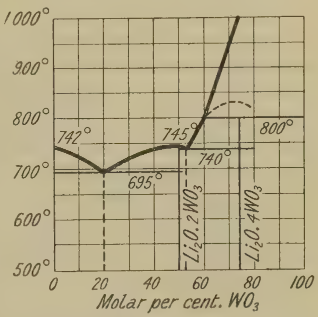


Fig. 25.—Freezing Points of the System: Li_2WO_4–WO_3.

A. Rosenheim and W. Reglin found the hydrate to be $Li_2WO_4.H_2O$, and that the salt in aq. soln. is strongly hydrolyzed. With atm. carbon dioxide, lithium carbonate and tungstic acid are formed. The salt is soluble in a soln. of lithium hydroxide, and on evaporating the soln., a non-crystallizable syrup is obtained.

Anhydrous **sodium tungstate,** Na_2WO_4, was obtained by E. F. Anthon,[3] E. Zettnow, and F. Ullik by fusing together eq. proportions of tungsten trioxide and the alkali hydroxide or carbonate. It was also produced by B. von Pawlewsky, by allowing the hydrate to stand for a long time over conc. sulphuric acid; by A. Riche, by allowing it to stand in vacuo; and by A. Riche, V. Forcher, B. von Pawlewsky, and R. Funk, by heating the hydrate over 100°. The preparation of the salt from wolframite, etc., has been discussed in connection with the extraction of tungsten (*q.v.*). It separates from its aq. soln. in the hydrated form. W. Jander and A. Winkel observed that the normal alkali tungstate is formed in aq. soln. when the $[H^{\cdot}]$-concentration lies between 10^{-14} and $10^{-6\cdot5}$; and the paratungstate $R_5(HW_6O_{21})$ when the conc. is between 10^{-65} and $10^{-6\cdot5}$.

The relations of sodium tungstate to water closely resemble those of sodium molybdate. The percentage solubility, S, found by R. Funk, was:

	−5°	0°	5°	6°	10°	20°	40°	80°	100°
S .	30·6	36·5	41·0	41·8	41·9	42·2	43·8	47·4	49·2
Solid phase	$10H_2O$			$2H_2O$					

There is an unstable form of the dihydrate with S=41·7 at −3·5°. The results are plotted in Fig. 26, where the dotted curve refers to sodium molybdate, the continuous curve to sodium tungstate. The anhydrous tungstate does not appear as a stable phase in the system below 100°. A. Riche obtained the *dihydrate,* $NaWO_4.2H_2O$, from a soln. of tungsten trioxide and sodium carbonate; and E. F. Anthon from a soln. of that oxide and sodium hydroxide, or from an aq. soln. of a previously melted mixture of wolframite and sodium carbonate. The dihydrate can be recrystallized from water. The conditions of stability are indicated in Fig. 26. R. Funk showed that below 6°, the aq. soln. furnishes crystals of the decahydrate: $Na_2WO_4.10H_2O$. Analyses of the dihydrate were made by E. F. Anthon, V. Forcher, R. Funk, E. Wegelin, J. C. G. de Marignac, A. Riche, and E. Zettnow.

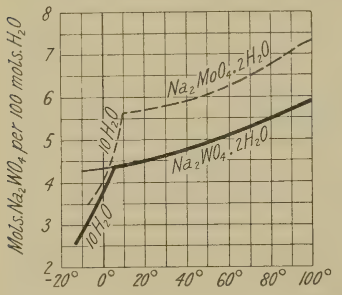


FIG. 26.—The Solubility of Sodium Tungstate in Water.

Anhydrous sodium tungstate furnishes white crystals; and when heated, the salt undergoes two transformations. H. E. Boeke showed that the changes are reversible. The molten liquid freezes at about 700°—f.p. Fig. 27. For reasons which will appear, H. E. Boeke called the salt in this state β-Na_2WO_4, and he observed that there is a **transition point** at 588°, involving the reversible change: $\beta\text{-}Na_2WO_4 \rightleftharpoons \gamma\text{-}Na_2WO_4$; and at 564°, γ-Na_2WO_4 passes into δ-Na_2WO_4 by a reversible process: $\gamma\text{-}Na_2WO_4 \rightleftharpoons \delta\text{-}Na_2WO_4$. The δ-form is stable at ordinary temp. According to N. Parravano, the transition points on the cooling curve for the $\beta \rightleftharpoons \gamma$ and the $\gamma \rightleftharpoons \delta$ transformations are respectively 585° and 568°; H. S. van Klooster gave respectively 589° and 572°; F. Hoermann, 590° and 583°; and K. Hüttner and G. Tammann found the $\gamma \rightleftharpoons \delta$ transition to occur at 570°—J. A. M. van Liempt gave 577°; and A. Hare, 579°. H. S. van Klooster and H. C. Germs found on the heating curve, 587° for the $\delta \rightleftharpoons \gamma$ transition point—J. A. M. van Liempt gave 588°—and 591° for the $\gamma \rightleftharpoons \beta$ transition point. The thermal value of the $\delta \rightleftharpoons \gamma$-transformation is much greater than that of the $\gamma \rightleftharpoons \beta$-transformation. Sodium sulphate shows a transition point at 239° in which what H. E. Boeke called α-Na_2SO_4 passes into ϵ-Na_2SO_4, the form stable at ordinary temp.

The reason the β-prefix is not here employed turns on the fact that on comparing the results with sodium sulphate with those obtained with the molybdate and tungstate, other forms may be subsequently discovered. The results with sodium sulphate, molybdate, and tungstate are summarized in Fig. 27, and in the following table showing the range of stability of the different forms, as well as their birefringence, b:

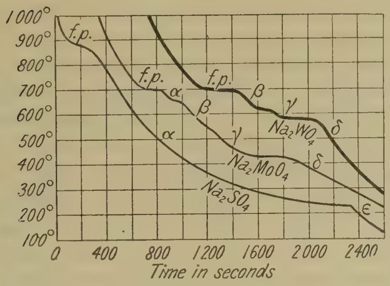


FIG. 27.—Cooling Curves of Sodium Sulphate, Molybdate, and Tungstate.

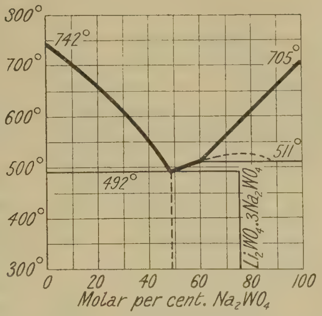
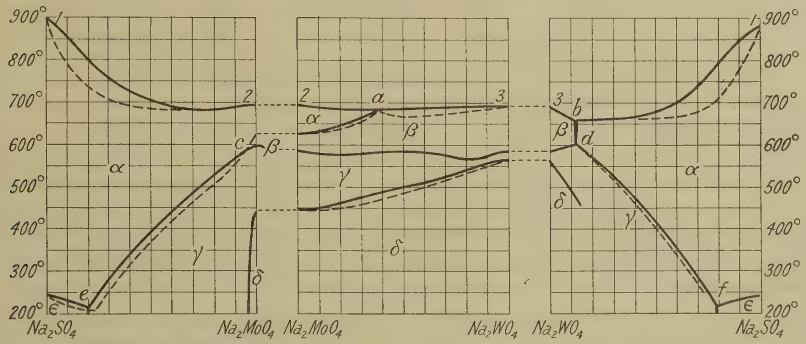


FIG. 28.—Freezing-point Curves of the System: Li_2WO_4–Na_2WO_4.

	Melting-point	α-crystals (b feeble)	β-crystals (b strong)	γ-crystals (b very strong)	δ-crystals (isotropic)	δ-crystals (b very strong)
Na_2SO_4 .	888°	888°–239°	,,	,,	,,	239°– . . .
Na_2MoO_4.	698°	—	698°–588°	588°–564°	564°– . . .	,,
Na_2WO_4.	692°	692°–619°	619°–587°	587°–431°	431°– . . .	,,

R. Lorenz and W. Herz made some observations on the transition temp. of sodium tungstate. The f.p. curve of the system, Li_2WO_4–Na_2WO_4, by J. A. M. van Liempt, is shown in Fig. 28. There is a simple eutectic at 491° and 45 molar per cent. of sodium tungstate. F. Hoermann's observations are summarized in Fig. 28. A compound of the two salts is formed with an incongruent m.p. at 511°. H. S. van Klooster and H. C. Germs' observations on the behaviour of each of the three salts—Na_2WO_4, Na_2MoO_4, and Na_2SO_4—in binary systems is illustrated by Figs. 29 to 31; and these diagrams are combined in Fig. 32 to represent the ternary system—Na_2SO_4–Na_2MoO_4–Na_2WO_4. H. E. Boeke, and P. Kordes also studied the system Na_2MoO_4–Na_2WO_4.



FIGS. 29, 30, and 31.—The Binary Systems Na_2SO_4–Na_2MoO_4, Na_2MoO_4–Na_2WO_4, and Na_2WO_4–Na_2SO_4.

The ordinary commercial salt is the dihydrate, and the white or transparent, nacreous, scaly **crystals** were described by L. N. Vauquelin and L. Hecht as four-sided plates, and by E. F. Anthon, A. Riche, and V. Forcher as rhombic plates. According to J. C. G. de Marignac, the rhombic bipyramids have the axial ratios $a:b:c=0{\cdot}8002:1:0{\cdot}6470$. F. Zambonini gave $0{\cdot}8013:1:0{\cdot}6524$, and for the optic axial angle, $2E=35°\ 20'$ for $\lambda=667$; 39° 30′ for Na-light; and 43° 40′ for $\lambda=533$. The crystals were also described by C. F. Rammelsberg, and E. Herlinger. According to F. W. Clarke and J. L. Davis, the **specific gravity** of the anhydrous salt is 4·1833 at 18·5° and 4·1743 at 20·5°; and that of the dihydrate is 3·2588 at 17·5° and 3·2314 at 18·5°. F. Zambonini gave 3·50 at 15°/15°. F. M. Jäger's values for the molten salt are indicated below; and he represented the sp. gr., D, at $\theta°/4°$ between 930° and 1595° by $D=3{\cdot}673-0{\cdot}0009275$, $(\theta-930)+0{\cdot}0_6337(\theta-930)^2$. The sp. gr. at 917° was 3·685; at 1128°, 3·502; and at 1330°, 3·356. W. Herz, and R. Lorenz and W. Herz made some observations on this subject. The sp. gr., D, of aq. soln. of the dihydrate with the following percentage proportion of Na_2WO_4, were measured by B. von Pawlewsky, who found:

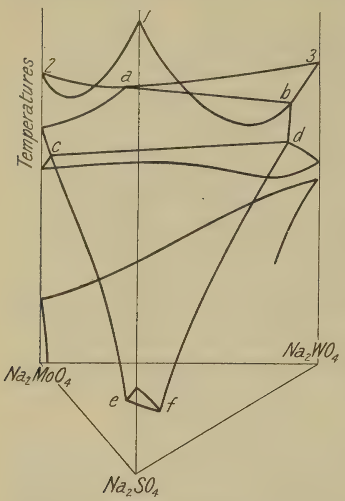


FIG. 32.—The Ternary System: Na_2SO_4–Na_2MoO_4–Na_2WO_4 at different Temperatures.

Na_2WO_4		2·21	6·25	10·08	14·44	20·59	25·46	32·68	38·43
D	20°/20°	1·02016	1·05831	1·09687	1·14392	1·21720	1·28143	1·38826	1·48595
	20°/4°	1·01837	1·05641	1·09486	1·14177	1·21483	1·27887	1·38539	1·48279

Observations were also made by I. Traube, and B. Franz. I. Traube found the drop-weight of the molten salt to be 259 referred to water 100 at 0°. F. M. Jäger gave the following values for the sp. gr. D, the **specific cohesion,** a^2 mgrm. per mm.; the **surface tension** σ dynes per cm.; and the **surface energy,** χ ergs per sq. cm. of the molten salt:

	710°	788°	1038·5°	1181·4°	1231·5°	1331·5°	1450°	1595°
D_2	3·893	3·812	3·576	3·461	3·424	3·355	3·282	3·208
a	10·65	10·60	10·34	10·15	10·00	9·76	9·44	9·02
σ	203·3	198·2	181·4	172·4	168·0	160·6	152·0	142·6
χ	3632	3591	3430	3332	3270	3168	3043	2899

R. Lorenz and W. Herz discovered some relations of the surface tension. J. J. Coleman found that the **diffusion** of 28, 25, and 17 per cent. of normal soln. of sodium molybdate, chromate, and tungstate respectively occurred in 30 days at 12·5°. H. Schulz and G. Jander observed that the diffusion coeff. of the tungstate ion in aq. soln. of sodium tungstate decreases considerably with increasing acidity of the soln., which is probably due to an increase in complexity of the ions according to some such scheme as $7WO_4''+8H^{\cdot}\rightleftharpoons W(WO_4)_6''''''+4H_2O$. In soln. $0{\cdot}1N$ in respect of a mineral acid and containing neutral salts, the degree of aggregation of the tungstate ion is 5 to 7 times that of the ion in alkaline soln. In soln. which contain no neutral salts, but are $0{\cdot}1N$ in respect of a mineral acid and have been boiled, the degree of aggregation is 9 to 11. G. Tammann found the **vapour pressure** of soln. with 19·62, 56·06, and 111·13 grms. of sodium tungstate in 100 grms. of water at 100° was 24·6, 85·3, and 197·1 mm. less than the value for water alone. E. F. Anthon, and V. Forcher observed that the salt melts at a red-heat, forming a clear liquid which, on cooling, solidifies to a crystalline mass. K. Hüttner and G. Tammann, H. E. Boeke, and N. Parravano gave 698° for the **melting point** of sodium tungstate; H. S. van Klooster, 700°; F. Hoermann, and J. A. M. van Liempt, 705°; and H. S. van Klooster and H. C. Germs, 694°. E. F. Smith gave for the m.p. of

$Na_2O.WO_3$, 665°; $5Na_2O.12WO_3$, 705·8°; $4Na_2O.10WO_3$, 680·8°; $9Na_2O.22WO_3$, 683·3°; and $Na_2O.4WO_3$, 706°. N. Parravano measured the f.p. curve of mixtures of sodium tungstate and tungsten trioxide, so far as the solubility of the trioxide allows—namely, $Na_2O : WO_3 = 1 : 2·5$; according to J. A. M. van Liempt, and N. Parravano, transformations—*vide supra*—occur at 588°, and 564°. The m.p. of sodium tungstate falls steadily with increasing additions of tungsten trioxide until it reaches the eutectic at 626°. It then rises to a maximum at 731°, corresponding with the pyrotungstate $Na_2W_2O_7$. From 626° to 588°, the mixtures are composed of α-Na_2WO_4 and $Na_2W_2O_7$; from 588° to 564°, they are composed of β-Na_2WO_4 and $Na_2W_2O_7$; and below 564°, of mixtures of γ-Na_2WO_4 and $Na_2W_2O_7$. The subsequent course of the curve indicates the possible existence of $Na_2W_5O_{16}$, but excludes the tritungstate $Na_2W_3O_{10}$. The results of F. Hoermann are summarized in Fig. 33. J. A. M. van Liempt gave 738° for the m.p. of sodium ditungstate, and 628° for the eutectic with normal tungstate; he also noted the lowering of the transition temp. of sodium tungstate by tungsten trioxide. E. Wegelin found that 0·5196 grm. of the dihydrate in 20 c.c. of water lowered the f.p. of water at 0·3°. This corresponds with a mol. wt. of 112·3. Other determinations gave analogous results. The theoretical mol. wt. for Na_2WO_4 is 294·1, hence the salt in aq. soln. probably furnishes three ions. W. G. Mixter gave for the **heat of formation** with powdered tungsten: $W+3Na_2O_2=Na_2WO_4+2Na_2O+231·2$ Cals.; $W+Na_2O+3O=Na_2WO_4+291$ Cals.; and $WO_3+Na_2O=Na_2WO_4+94·1$ Cals.; and L. Pissarjewsky gave H_2WO_4aq.$+2NaOH$aq.$=Na_2WO_4$aq.$+H_2O+13·694$ Cals. A. Hare gave 9·51 Cals. per mol for the energy of the transformation at 579°.

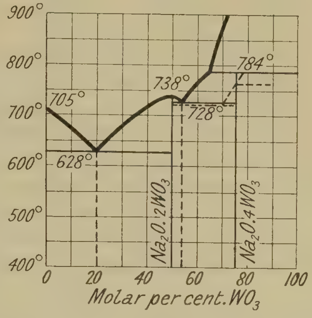


FIG. 33.—Equilibrium Curves of Mixtures of Sodium Tungstate and Tungsten Trioxide.

B. von Pawlewsky found the **index of refraction,** μ, of soln., at 20°, with the following percentage proportions of sodium tungstate, to be:

Na_2WO_4	2·21	6·25	10·08	14·44	20·59	25·46	32·68	38·43
μ	1·33586	1·34065	1·34516	1·35064	1·35933	1·36648	1·37306	1·38890

H. Schulz and G. Jander found that with increasing acidity, the optical absorption limit of the soln. moves towards the region of longer wave-lengths. This is taken to indicate an aggregation of the anions. O. H. Wagner found for the index of refraction, μ, of the molten salt for wave-lengths λ at $\theta°$: $\mu=a-b(\theta-750)$, so that

λ	0·670	0·610	0·589	0·579	0·546	0·436
a	1·574	1·580	1·588	1·589	1·595	1·615
b	0·00021	0·00024	0·00026	0·00021	0·00020	0·00011

or $\mu=2·6531+1·0562\lambda/\{\lambda^2-(1·777)^2\}$. For the luminescence in **X-rays,** *vide infra*, calcium tungstate. P. Krishnamurti examined the **Raman effect.**

P. Walden, J. Eltzbacher, and H. Grossmann and H. Krämer measured the **electrical conductivity** of soln. of sodium tungstate; and C. Watkins and H. C. Jones gave for the conductivity, μ mhos, of soln. with a mol of the salt in v litres of water:

	v	4	8	16	32	128	512	1024
μ	0°	63·5	74·4	88·2	93·3	105	114	116
	15°	107	120	135	143	162	175	178
	25°	—	151	169	180	203	221	225
	35°	—	183	206	219	249	271	272

W. V. Bhagwat and N. R. Dhar gave for the eq. conductivity, λ, of a soln. with a mol of the salt in v litres at 21°:

v	8	16	32	64	128	256	512	1024
λ	77·6	82·9	87·3	91·3	95·3	99·1	101·3	103·9

so that $\mu_{1024}-\mu_{32}=16{\cdot}6$; and P. Walden gave $\mu_{1024}-\mu_{32}=21{\cdot}5$. F. M. Jäger and B. Kapma represented the mol. conductivity of the fused salt at $\theta°$ between 750° and 501° by $\mu=83{\cdot}50+0{\cdot}185(\theta-750)$; and the resistance, R ohms, and sp. gr. D, are :

	752·5°	958°	1066°	1209°	1361·5°	1412°	1501°
D .	3·843	3·648	3·554	3·443	3·339	3·308	3·258
R .	0·1706	0·1194	0·0996	0·0804	0·0702	0·0650	0·0628

The subject was discussed by W. Biltz and W. Klemm. G. Gore obtained black matter at the cathode during the **electrolysis** of fused sodium tungstate, and a gas was given off at the anode. E. Schaefer, and M. Kröger obtained colloidal tungstic acid (*q.v.*) by the electrolysis of soln. of sodium tungstate ; and A. Lottermoser obtained paratungstate and other complex tungstates. P. Burckhard found that the molten salt conducts the electric current, forming oxygen at the anode, and at the cathode, a mass of tungsten hemipentoxide—*vide supra*, the extraction of tungsten. According to E. F. Smith, neutral soln. of the tungstates are not affected by the electric current, but J. Eltzbacher, E. Schaefer, and E. F. Smith made observations on the electrolysis of acidified soln. of sodium tungstate, and found that tungstic acid, at the cathode, is reduced to the blue oxide. R. G. Wells said that the conductivity of the aq. soln. does not change with time.

F. Wöhler said that the salt is not decomposed when it is heated in **hydrogen ;** and E. Bouchhaus studied the reaction. V. Spitzin observed that neutral sodium tungstate is reduced by hydrogen at 900° in accord with $Na_2WO_4+4H_2=2Na+W+4H_2O$; and J. A. M. van Liempt said that the reduction at 1100° proceeds: $Na_2WO_4+3H_2=W+2NaOH+2H_2O$. R. Funk said that the dihydrate is stable in **air,** but V. Forcher observed that efflorescence occurs in dry air. According to L. N. Vauquelin and L. Hecht, 100 parts of **water** dissolve 25 parts of the salt in the cold, and 50 parts when boiling; and E. F. Anthon gave, respectively, 100 and 200. A. Riche reported that 100 parts of water dissolve 40·98 parts of salt at 0° ; 55·25 parts at 15° ; and 123·4 parts at the b.p. ; and R. Funk, that 100 parts of water dissolve 90·09 parts of salt at 21°, and 123·4 at the b.p.—*vide supra*. E. F. Anthon said that the soln. has a bitter, rough, saline taste, and an alkaline reaction. B. Kellner observed that the salt dissolves more easily in **hydrogen dioxide** than it does in water, and the soln. is yellow, and reacts acid. W. K. van Haagen and E. F. Smith found that the heated tungstate is attacked with difficulty by **hydrogen fluoride.** V. I. Spitsin and L. Kaschtanoff said that with **hydrogen chloride,** volatile tungsten dioxydichloride and sodium chloride are formed. According to A. Riche, and E. Zettnow, a soln. of the salt is decomposed by strong **acids** as well as by boric, sulphurous, carbonic, oxalic, and acetic acids, and, added V. Forcher, by carbon dioxide. The action of phosphoric acid has been discussed by C. Scheibler, J. Lefort, etc.—*vide infra*, phosphotungstates—H. Rose said that with a soln. of a tungstate, phosphoric acid gives a white precipitate, soluble in excess ; and E. Zettnow added that the normal alkali tungstates do not precipitate orthophosphoric acid, and by quickly transforming that acid into metaphosphoric acid, hinder the precipitation of tungstic acid by other acids. F. J. Factor found that when the soln. is warmed with **sodium thiosulphate,** a mixture of tungsten dioxide, trioxide, and the lower oxides is precipitated ; and **alkali sulphites** give no blue coloration with the hot soln., but if a little hydrochloric acid be present, a feeble blue colour may appear. A. Rosenheim observed that the tungstates seem to form unstable complex salts when treated with **sulphur dioxide.** F. Bourion said that chlorine mixed with the vapour of **sulphur dichloride** drives out all the tungsten as volatile chloride from sodium tungstate at 180°–450°. W. I. Baragiola showed that when a soln. of sodium tungstate is treated with **ammonium chloride,** various acid tungstates are formed—namely, $3(NH_4)_2O.2Na_2O.15WO_3.25H_2O$; $4(NH_4)_2O.2Na_2O.15WO_3.21H_2O$; and $6(NH_4)_2O.2Na_2O.20WO_3.24H_2O$. F. Wöhler, and E. F. Anthon supposed that ammonium salts with conc. soln. of sodium tungstate give the ammonium salt, but A. Laurent, and W. Lotz said that a double salt is produced—*vide infra*. H. Traube obtained trigonal, bipyramidal crystals of probably an isomorphous mixture **lithium sodium 1 : 3-tungstate,** $Li_2WO_4.3Na_2WO_4.12H_2O$, from a soln. of equimolar proportions of the two salts. The axial ratios are $a : c = 1 : 0{\cdot}8947$, and $\alpha = 100° 34'$. The optical character is negative. L. Kahlenberg and W. J. Trautmann found that sodium tungstate reacts with silicon with difficulty, forming no free metal or silicide. H. S. van Klooster examined fused mixtures of sodium metasilicate and tungstate. The two salts are practically immiscible in the liquid state, and quite immiscible in the solid condition. The fragment of the equilibrium diagram which was explored is shown in Fig. 34. J. A. M. van Liempt examined the sp. gr., D, the viscosity, η, and the sp. electrical conductivity, K, of soln. of mixtures of sodium orthosilicate, Na_4SiO_4, and sodium tungstate, Na_2WO_4, and found that the curves show no maxima or minima at 30°. The results were :

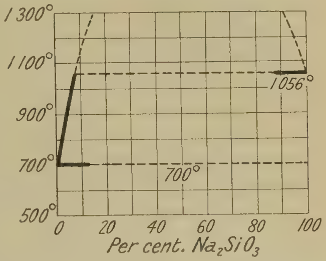


FIG. 34.—Equilibrium Diagram of the System : Na_2WO_4–Na_2SiO_3.

Na_2WO_4 .	0	2	4	6	8	10 vol. per cent.
D . .	1·193	1·206	1·218	1·230	1·242	1·225
η . .	2·888	2·579	2·389	2·062	1·881	1·671
K . .	0·1517	0·1317	0·1241	0·1154	0·1057	0·0910

The action of many reagents on aq. soln. has been discussed in connection with the analytical reactions of tungsten. P. Hautefeuille and A. Perrey, and H. Corimboeuf discussed its use as *un agent mineralisateur*—**6**. 40, 17 and 22—in the synthesis of silicate minerals, and in the conversion of **silica.** H. S. van Klooster found that sodium tungstate and sodium silicate, Na_2SiO_3, are practically immiscible below 1100° ; and they are completely immiscible in the crystalline state. A. Riche, and V. Forcher found that alcohol precipitates crystals of the salt from its aq. soln., and that the salt is insoluble in **alcohol.** O. Maschke showed that strongly alkaline soln. are coloured blue by **organic compounds** owing to reduction ; and R. E. Liesegang found that a mixture of sodium tungstate with a soln. of citric acid is sensitive to light, and on isolation, acquires a blue colour. The coloration is not produced by sodium tungstate alone nor in the presence of acetic acid, sodium oxalate, stannous chloride, or ammonium thiocyanate. According to J. H. Long, the optical rotation of a soln. of potassium antimonyl tartrate is raised by the addition of sodium tungstate, very little tungstic acid is precipitated. D. Gernez also observed that the optical activity of several organic substances is raised by sodium tungstate, itself optically inactive. A. V. Dumansky and S. I. Diatschkovsky observed its action on the activity of tartaric acid. J. Lefort studied the action of quinine on normal alkali tungstate. C. N. Fenner, and C. J. van Nieuwenburg and C. N. G. de Nooijer discussed its catalytic action on the transformations of silica (*q.v.*). F. Mauro and R. R. Panebianco discussed the reduction of tungstic acid or tungstates in hydrofluoric acid soln. by metals. F. Hoermann's observations, Fig. 28, show that a compound **lithium sodium tungstate,** $Li_2WO_4.3Na_2WO_4$, is formed with an incongruent m.p. of 511°.

E. F. Anthon prepared anhydrous **potassium tungstate,** K_2WO_4, by crystallization from a filtered soln. of tungstic acid in soln. of potassium hydroxide or carbonate. J. C. G. de Marignac said that the anhydrous salt is always obtained when the hot, sat. soln. is cooled, or evaporated hot. F. Ullik added that if the alkali-lye contains sodium, a mixed sodium potassium tungstate is formed. E. F. Anthon, E. Zettnow, and F. Ullik melted equimolar proportions of potassium carbonate and tungsten trioxide at a red-heat. The mass on cooling disintegrates to a powder, indicating that polymorphic transformations are involved. J. C. G. de Marignac found that if the aq. soln. be evaporated over sulphuric acid, below 10°, monoclinic prisms and plates of the dihydrate, $K_2WO_4.2H_2O$, are formed ; they have the axial ratios

$a:b:c=0{\cdot}9998:1:0{\cdot}7830$, and $\beta=110°\ 57'$; and they effloresce in dry air particularly if warmed, and deliquesce rapidly in moist air. A. Riche reported a *monohydrate*, $K_2WO_4.H_2O$, but he probably mistook a partially effloresced dihydrate for the monohydrate. E. F. Anthon's hexagonal *pentahydrate*, $K_2WO_4.5H_2O$, was, according to F. Ullik, a mixed sodium potassium tungstate. As stated by S. Surawicz, the assumption of water produces no change in the crystal system, for J. C. G. de Marignac showed that the acicular crystals of the anhydrous salt are monoclinic prisms with the axial ratios $a:b:c=1{\cdot}9702:1:1{\cdot}2341$, and $\beta=113°\ 15'$. Twinning occurs about the (001)-plane. J. W. Retgers found that the crystals are isomorphous with those of potassium sulphate, selenate, and molybdate. J. W. Retgers found that two kinds of crystals are formed during the evaporation of aq. soln. —(i) slender needles which exhibit feeble polarization, and are coloured green by potassium manganate with which they are isomorphous; and (ii) prisms which exhibit strong polarization and are not coloured by potassium manganate. J. W. Retgers considered that the first kind of crystals are rhombic and are pseudohexagonal; and the second kind are probably monoclinic. It is not improbable that anhydrous and dihydrated crystals are here in question. F. M. Jäger found the sp. gr. of the molten salt at $\theta°/4°$, between 925° and 1520·3°, to be best represented by $D=3{\cdot}113-0{\cdot}00082(\theta-1000)+0{\cdot}0_6162(\theta-1000)^2$—*vide infra* for data. F. M. Jäger and J. Kahn, and W. Herz made observations on this subject. I. Traube found the sp. gr. of soln. with 2·42, 6·57, 8·72, and 16·19 per cent. of the salt to be respectively 1·0202, 1·0575, 1·0781, and 1·1518, at 15°. I. Traube found the drop-weight of the molten salt at its m.p. to be 170 when that of water at 0° is 100. F. M. Jäger found the sp. gr., D, referred to water at 4°, the specific cohesion, a^2 mgrm. per mm.; the surface tension, σ dynes per cm.; and the surface energy, χ ergs per sq. cm., of the molten salt to be:

D_1	925·0°	1051·5°	1183·2°	1284·0°	1408·5°	1520·3°
a .	10·34	9·69	9·21	8·78	8·30	7·89
σ .	161·0	145·9	134·1	124·6	114·3	105·6
χ .	3531	3275	3076	2908	2723	2560

R. Lorenz and W. Herz discussed some relations of the surface tension. G. Tammann found the vapour pressure of soln. 19·71, 51·63, 81·77, and 156·52 grms. of the normal salt in 100 grms. of water at 100° to be respectively 17·6, 52·0, 96·9, and 215·4 mm. below that of water at 100°. F. Ullik, and J. C. G. de Marignac observed that when the salt is heated, there is a violent decrepitation attended by the loss of 0·25 to 0·50 per cent. of included water; the salt readily fuses at a red-heat without suffering any further loss. As indicated above, the shattering of the cooling solid indicates a transformation from one form to another. K. Hüttner and G. Tammann observed a transformation on the cooling curve occurs between 200° and 300°; and M. Amadori gave 575°, F. Hoermann, 338°; while H. S. van Klooster obtained 388° on the heating curve. K. Hüttner and G. Tammann gave 926° for the m.p.; J. A. M. van Liempt, 926° in one case and 933° in another; M. Amadori, 894°; F. Hoermann, 921°; and H. S. van Klooster, 921°. J. A. M. van Liempt found that potassium tungstate is not reduced by hydrogen at 1100°, but it volatilizes unchanged. For the luminescence in X-rays, *vide infra*, calcium tungstate. J. A. M. van Liempt measured the f.p. of mixtures of potassium tungstate and tungsten trioxide so far as the solubility of the trioxide allows—namely $K_2O:WO_3=1:2{\cdot}5WO_3$. There is a eutectic at 584° with 50 per cent. WO_3. F. Hoermann's results are shown in Fig. 35. J. A. M. van Liempt found that with the system

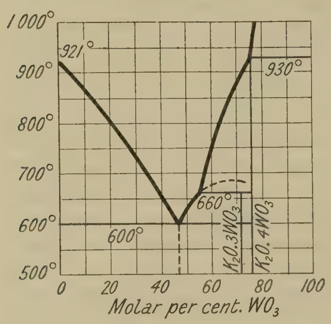


FIG. 35.—Freezing-point Curve of the System: K_2WO_4–WO_3.

Li_2WO_4–K_2WO_4, there is formed a compound **lithium potassium tungstate,** $Li_2WO_4.K_2WO_4$, melting at 632°, Fig. 36. It gives a simple eutectic with 70 per cent. of lithium tungstate at 579°, and with 40 per cent. lithium tungstate at 607°. J. A. M. van Liempt's curve for mixtures of sodium and potassium tungstates is shown in Fig. 37. There is a minimum in the curve with 20 per cent. of the potassium salt. According to M. Amadori, the f.p. curve of the binary system

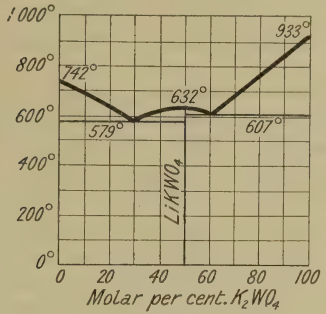


FIG. 36.—Freezing-point Curve of the System: Li_2WO_4–K_2WO_4.

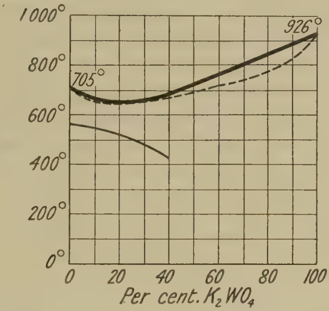


FIG. 37.—Freezing-point Curve of the System: Na_2WO_4–K_2WO_4.

K_2SO_4–K_2WO_4, Fig. 38, is continuous with a slight minimum 10° below the m.p. of the tungstate. The transformation point of the tungstate is not visible with mixtures containing over 15 molar per cent. of sulphate. The transformation of the sulphate follows a curve descending to 482° for mixtures containing 50 molar per cent. below which point it can no longer be followed. The f.p. curve is also continuous in the system K_2CrO_4–K_2WO_4, Fig. 39, and it is intermediate between the m.p. of the two salts. The transformation points follow curves rising to the transformation points of the salts above, but were not detected with mixtures containing between 15 and 40 per cent. of chromate. The curve in the system

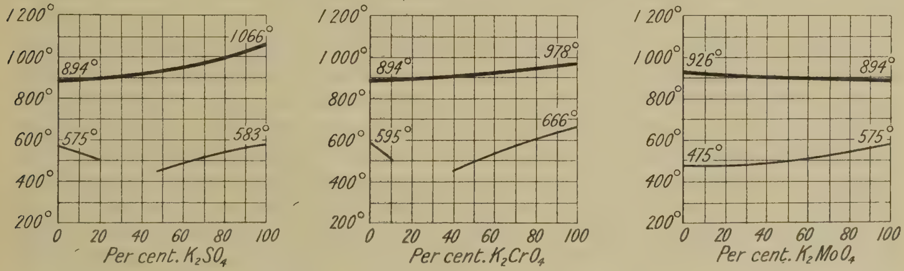


FIG. 38, 39, and 40.—Freezing-point Curve of Binary Mixtures of Potassium Tungstate with Potassium Sulphate, Chromate and Molybdate.

K_2MoO_4–K_2WO_4, Fig. 40, is almost a straight line between the m.p. of the two salts. The transformation point can be detected only with mixtures rich in one or other constituent. E. Blanc found that a 0·0162*N*-soln. of potassium tungstate is hydrolyzed 0·011 per cent. at 25°. J. A. M. van Liempt found the sp. gr. and viscosity curves of mixtures of potassium tungstate and potassium metasilicate, K_2SiO_3, gave similar results to those obtained with sodium tungstate and orthosilicate—*vide supra*. J. A. M. van Liempt observed that whilst sodium tungstate is reduced by hydrogen at 1100°, this is not the case with potassium tungstate. W. K. van Haagen and E. F. Smith found that potassium tungstate is attacked with difficulty by hydrofluoric acid. W. I. Baragiola treated soln. of potassium tungstate with ammonium chloride and obtained the salts $4\{\frac{1}{4}(NH)_4.\frac{3}{4}K\}_2O.11WO_3.10H_2O$; and

$2\{\frac{2}{3}(NH_4).\frac{1}{3}K\}_2O.5WO_3.8H_2O$. H. Traube obtained crystals of probably an isomorphous mixture of **sodium potassium 2 : 1-tungstate,** $K_2WO_4.2Na_2WO_4.14H_2O$.

Although **cuprous tungstate,** Cu_2WO_4, has not been prepared, H. Schultze[4] obtained what appeared to be a **cuprosic tungstate** by melting together a mixture of sodium tungstate, cuprous chloride, and sodium chloride (2 : 3 : 4) and extracting the cold mass with nitric acid. There remained white, and yellowish-brown, quadratic prisms. E. Zettnow obtained a pale brownish-red, crystalline powder of $Cu_2WO_4.2CuWO_4$, by fusing a mixture of equimolecular parts of copper sulphate and sodium tungstate, and leaching the cold product with water. The product was oxidized by nitric acid with the evolution of nitric oxide.

J. D. Whitney described a mineral from La Paz, California, which he called **cuproscheelite ;** M. Adam called it **cuprotungstate.** It occurred as a pistachio-green, olive-green, or leek-green, granular, crystalline mass, or in crusts. It was reported in the copper mines of Llamuco, Chili, by I. Domeyko ; in the Pot mine, S.W. Africa, by H. Traube ; and at Yeoral, N.S.W., by G. W. Card. The analyses by J. D. Whitney, and I. Domeyko show that it is a mixture of calcium and copper tungstates, and it can be represented by the formula $(Ca,Cu)WO_4$. According to L. Michel, and F. Fouqué and A. Michel-Lévy, the mineral can be synthesized by melting together a mixture of cupric chloride and sodium tungstate with an excess of sodium chloride. After washing the cold product with water, there remain pale green prisms and octahedra, which polarize light strongly.

G. Tammann observed that when a mixture of equimolecular proportions of cupric oxide and tungsten trioxide is heated, the formation of **copper tungstate,** $CuWO_4$, proceeds actively between 600° and 800°. According to E. F. Anthon, when a cupric salt is added to a soln. of normal potassium tungstate, a light green powder of copper tungstate is precipitated. When dried in air, its composition corresponds with the *dihydrate*, $CuWO_4.2H_2O$. When the dihydrate is heated, it turns yellowish-brown in colour ; fuses at a red-heat ; and, on cooling, it solidifies to a chocolate-coloured, crystalline mass containing cavities with crystalline geodes. The crystals are wine-yellow, transparent, six-sided prisms. G. Tammann gave 12·1 Cals. per mol for the heat of formation of the anhydrous salt, and 19·0 Cals. per mol for that of the dihydrate. R. E. Liesegang found that copper tungstate is not sensitive to light. For the luminescence in X-rays, *vide infra*, calcium tungstate. E. F. Anthon reported that the precipitated salt before ignition is insoluble in water, but after continued washing, it is peptized, and passes through the filter-paper rendering the filtrate turbid. Copper tungstate dissolves in phosphoric acid and acetic acids, and in aq. ammonia, but it is insoluble in oxalic acid. H. Schiff found that the soln. of copper tungstate in aq. ammonia is a corrosive liquid, which, when slowly evaporated, forms a dirty blue, crystalline crust of **copper diammino-tungstate,** $CuWO_4.2NH_3.H_2O$. Alcohol added to the ammoniacal soln. precipitates the salt as an amorphous powder. When dried over sulphuric acid, the salt loses its water without changing its form. S. H. C. Briggs prepared **copper tetrammino-tungstate,** $CuWO_4.4NH_3$, by precipitating a hot soln. of 7·5 grms. of copper sulphate with 10 grms. of dihydrated sodium tungstate, washing the precipitate by decantation, and dissolving it in 20 c.c. of cold, conc., aq. ammonia. A similar soln. was obtained by treating 13 grms. of dihydrated sodium tungstate with nitric acid, dissolving the washed tungstic acid in 20 c.c. of conc., aq. ammonia and adding it to an ammoniacal soln. of copper sulphate. Either of these soln. is filtered into a bottle, and a layer of alcohol allowed to diffuse slowly into the ammoniacal soln. during several weeks while the bottle is tightly closed. This prevents the escape of ammonia and avoids the formation of paratungstate. Blue crystals of the tetrammine slowly deposit. The blue crystals give off ammonia at ordinary temp. ; they dissolve in a small proportion of water ; and are easily dissolved by dil. aq. ammonia. No *ammonium copper tungstate* is formed however large an excess of ammonium tungstate is employed.

F. Wöhler and F. Rautenberg reported **silver subtungstate,** $Ag_4O.2WO_3$, to be formed by a method similar to that employed for silver submolybdate (*q.v.*); but W. Muthmann showed that in all probability the subtungstate is a mixture of silver and normal **silver tungstate,** Ag_2WO_4. E. Zettnow, and E. F. Smith and R. H. Bradbury prepared the normal salt by treating a soln. of the normal sodium salt with silver nitrate. The white precipitate soon becomes yellow. It can be washed without peptization. It should be prepared in darkness, and dried at 110° to 120°. It is not hygroscopic. It melts below redness to form a dark red liquid, which crystallizes on cooling. The salt is very sparingly soluble in water; and it is decomposed by nitric acid, and by a hot soln. of sodium chloride. The salt is decomposed by heat and is not a suitable form in which to precipitate tungstates for analytical work. A soln. of the normal salt in aq. ammonia, when evaporated over a mixture of quicklime and ammonium chloride, was found by O. Widman to furnish tabular crystals of **silver tetramminotungstate,** $Ag_2WO_4.4NH_3$. It is also obtained as a white powder by the action of ammonia gas on silver tungstate. When the tetrammine is heated over 60°, all the ammonia is expelled. The aq. soln. decomposes rapidly. P. Ray and J. Dasgupta prepared a complex with hexamethylenetetramine.

Normal **calcium tungstate,** $CaWO_4$, is represented by the mineral **scheelite**; and this played an important part in the history of our knowledge of tungsten. The observations of C. W. Scheele,[5] J. G. Wallerius, A. G. Werner, C. von Linnæus, A. Cronstedt, D. L. G. Karsten, R. J. Haüy, A. Breithaupt, and C. C. Leonhard have been previously described; the review of the occurrence of tungsten includes that of scheelite. For **powellite,** $Ca(W,Mo)O_4$, *vide* calcium molybdate. According to F. de Carli, when a mixture of tungsten trioxide and calcium oxide is heated, evidence of a thermal effect appears at 245°; and D. Balareff said that the maximum rise of temp. occurs at 750°. W. Jander said that the reaction with calcium carbonate begins at 600°. According to G. Tammann, the formation of calcium tungstate proceeds actively between 580° and 950°. When calcium carbonate is heated with tungsten trioxide, carbon dioxide comes off at temp. over 510°. E. F. Anthon, and J. Lefort obtained calcium tungstate as a precipitate by mixing soln. of normal potassium or sodium tungstate with a feebly acidified soln. of calcium chloride. A. de Schulten heated in a water-bath soln. of 10 grms. of anhydrous calcium chloride in 3 litres of water and 1 c.c. of conc. hydrochloric acid, and gradually added, drop by drop, a soln. of 3 grms. of ordinary sodium tungstate. Crystals of calcium tungstate gradually collect on the bottom of the vessel. The crystals are larger if more acid is used, but they are then coloured yellow. L. Weiss added a soln. of calcium chloride to an ammoniacal soln. of tungstic acid, almost neutralized with acid, so long as precipitation occurred; the liquid was then feebly acidified and the precipitated calcium tungstate washed and dried. E. Kunau used a similar process. N. S. Manross prepared the salt by melting a mixture of sodium tungstate and calcium chloride at a red-heat, and extracting the cold product with water. L. Michel found that if an excess of sodium chloride is also used with the mixture, larger crystals are obtained. H. Debray obtained crystals of scheelite by heating a mixture of amorphous calcium tungstate and quicklime in a current of hydrogen chloride; and A. Cossa imitated the crystals of the scheelite of Traversella by heating under sodium chloride a mixture of amorphous calcium tungstate and a little didymium salt. H. Traube obtained the crystals as a sublimate by heating to a high temp. a mixture of the tungstate with sodium and potassium chlorides. F. Zambonini found that the processes of A. Macé, and A. Drevermann, used for the synthesis of anglesite—7. 47, 30—give the best results in preparing crystals of scheelite. For the preparation of phosphorescent calcium tungstate, *vide infra.* Analyses were reported by A. Carnot, N. S. Manross, J. Lefort, A. Roemer, M. H. Klaproth, R. Brandes and C. F. Bucholz, B. Setlik, C. F. Rammelsberg, F. A. Bernoulli, G. T. Bowen, F. A. Genth, I. Domeyko, A. Delesse, M. Choubine, J. J. Berzelius, D. Lovisato, C. G. Hoffmann, L. Colomba, S. Traverso, C. Schmidt, W. Florence, J. Block, A. Lacroix, A. M. Findlayson, J. Eyerman, B. K. Almström, and G. Carobbi. Copper, manganese, iron, and tin oxides may be present, as well as some chlorine and fluorine. According to H. Traube, molybdenum is usually present in scheelite, and it replaces part of the tungsten. In the specimens he examined, up to 8·23 per cent. MoO_3 was observed. The amount varies with crystals from the same localities. The white and yellow varieties contained least, and the dark coloured varieties most. The proportion of molybdenum probably affects the angles of the crystals. L. G. Igelström also reported the presence of molybdenum in scheelite; A. Carnot found about 0·4 per cent. of tantalic oxide in scheelite from Meymac, Correze; and A. Cossa found didymium, cerium, and lanthanum oxides; the spectra showed strong absorption bands of these oxides; and C. de Rohden found the presence of samarium, erbium, terbium, europium, neodymium, and praseodymium salts in scheelite. G. T. Lindroth found copper, molybdenum, and bismuth; G. Carobbi, molybdenum, tantalum, columbium, and the rare earths. Precipitated calcium tungstate is an amorphous white powder; scheelite occurs in white, yellowish-white, pale yellow, brownish-yellow, greenish-yellow, reddish-yellow or orange-yellow granular masses, in reniform masses with a columnar structure, or in tetragonal, bipyramidal crystals which, according to H. Dauber, have the axial ratio $a:c=1:1·5356$; H. Traube gave 1 : 1·5315; H. Dauber, 1 : 1·5329 to 1·5355; G. vom Rath, 1 : 1·5364; V. R. von Zepharovich, 1 : 1·5349; L. Colomba, 1 : 1·53798; and F. Zambonini, 1 : 1·5300. There may be pyramidal hemihedrism. The habit may be octahedral or tabular. There may be contact and penetration twinning about the (100)-plane. The (001)-faces may be rough, and the (101)-faces striated. The faces of the twins may show feather-like striations meeting in a median line. The (111)-cleavage is most distinct; the (101)-cleavage is interrupted. E. Hugi studied the corrosion figures. The crystals were described by F. A. Genth, M. Bauer, H. Traube, C. F. Rammelsberg, C. Schmidt, G. Flink, L. Colomba, J. Block, C. Anderson, A. Serra, S. Koch, T. Hiortdahl, A. Russell, A. Roemer, A. de Schulten, E. Hugi, P. Berberich, etc. J. W. Retgers discussed the isomorphism of the alkaline earth molybdates, tungstates, sulphates, selenates, and chromates. R. G. Dickinson found that the X-radiogram corresponds with a face-centred lattice with the atoms so located as to give a diamond arrangement. The arrangement of the atoms is the same as in the case of lead molybdate (*q.v.*) with calcium in place of lead, and tungsten in place of molybdenum—Fig. 23, **11**. 61, 11. The calculated sp. gr. is 6·06, and the edge of the unit cell of 8 mols. is $a=22·80$ A. F. M. Jäger and H. Haga made some observations on the X-radiograms, and attributed the high degree of symmetry to twinning. L. Vegard gave for the lattice dimensions of scheelite, which is of the rutile type, $a=7·44$ A., and $c=11·35$ A., and for the ionic diameter 1·125 A. M. L. Huggins made some observations of the structure of the crystals. E. Tiede and A. Schleede also studied the X-radiogram. T. Barth said that the unit tetragonal cell contains four mols. of $CaWO_4$ and has $a=5·26$ A., $c=11·41$ A., and $a:c=1:2·17$; on the other hand, L. Vegard inferred that the unit cell has 8 mols. $CaWO_4$, $a=7·44$ A., $c=11·35$ A., and $a:c=1:1·537$; L. Vegard and A. Refsum gave $a=7·44$ A., $c=11·35$ A.; the radius of the oxygen atom is 1·125 A., of the metal in WO_4, 1·04 A., and of the positive ion, 1·11 A. N. S. Manross gave 6·076 for the sp. gr. of calcium tungstate; A. de Schulten, 5·542 at 15°; C. J. B. Karsten, 6·04; F. A. Bernoulli, 6·02; C. F. Rammelsberg, 6·03; and F. Zambonini, 6·0620. F. A. Henglein discussed the mol. vol. —47·53. H. Traube found that the sp. gr. of the samples of scheelite he examined ranged from 5·88 to 6·12. J. J. Saslawsky calculated a contraction of 0·51 to 0·54 in the formation of scheelite from its elements. The hardness ranges from 4·5 to 5·0. E. Cane gave 0·104 for the sp. ht. M. D. Draper, A. D. Cox, and J. J. Rubber devised methods for estimating the percentage amount of tungsten trioxide in scheelite ores from sp. gr. determinations. M. D. Draper found:

Sp. gr.	3·00	3·50	4·00	4·50	5·00	5·50	6·00
WO_3	15·40	31·20	44·80	56·20	65·40	72·00	78·20

E. Jannetaz found the ratio of the heat conductivities of scheelite a/γ to be 0·9. D. Vorländer and H. Hempel observed no transformation points on the heating curve of calcium tungstate. H. Kopp gave 0·0927 for the sp. ht. between 19° and 58°. G. Tammann gave 39·8 Cals. per mol for the heat of formation from its constituent oxides. A. des Cloizeaux gave for the indices of refraction for red-light, ω=1·918–1·919, and ϵ=1·934–1·935 ; the optical character is positive. F. Zambonini gave for the light of wave-length λ,

λ . .	667	C-line	623	D-line	570	533	E-line	475
ω . .	1·9107	1·9124	1·9159	1·9200	1·9208	1·9273	1·9298	1·9344
ϵ . .	1·9263	1·9281	1·9321	1·9365	1·9375	1·9442	1·9368	1·9525
ϵ—ω . .	0·0156	0·0157	0·0162	0·0165	0·0167	0·0169	0·0170	0·0181

Hence the dispersion increases regularly from the red to the violet ; and it is stronger for the ordinary than for the extraordinary ray. F. Zambonini also examined the optical constants of mixtures of calcium and cerous tungstates, and showed that the two salts furnish isomorphous mixtures. E. F. Anthon said that calcium tungstate is insoluble in water ; but J. Lefort found that 100 parts of water at 15° dissolve 0·2 part of calcium tungstate. E. F. Smith and R. H. Bradbury did not get good results when, for analytical purposes, the tungstates are precipitated in the form of calcium tungstate. E. F. Smith found that scheelite dissolves when it is heated with sulphur monochloride.

G. Ogden prepared calcium tungstate for use as screens which become luminous when exposed to X-rays. The luminescence was discussed by E. Kunau, T. H. Tsao, and F. R. van Horn. W. Arnold found that while the mineral scheelite exhibits a strong blue fluorescence when exposed to X-rays, the freshly-prepared and ignited calcium tungstate is only feebly luminescent, but it is more luminescent if it has been heated in the oxhydrogen flame. A solid soln. of copper tungstate in calcium tungstate is as luminous as scheelite ; manganese tungstate acts like the copper salt. The tungstates of sodium, potassium, strontium, barium, and zinc ; wolframite, ferberite, and the different tungstate-bronzes, are not luminous when exposed to the X-rays. K. Keilhack, F. Dreuschuch, R. J. Strutt, K. Endell, G. F. Kunz and C. Baskerville, P. Schuhknecht, F. E. Swindells, and C. H. Boissevain and W. F. Drea also studied the X-ray luminescence of the alkaline earth tungstates. W. Ducca, and W. Löwinthal studied the action of luminophores—*e.g.* traces of manganese, copper, or bismuth salts—in enhancing the fluorescence of calcium tungstate when exposed to X-rays. The presence of $\frac{1}{12,000}$th part of a bismuth salt gave the best results. The spectrum of the blue fluorescence of calcium tungstate containing a trace of a bismuth, manganese or copper salt shows feeble spectral bands in the blue violet ; and when the tungstate contains a trace of a silver, gold, nickel, cadmium, antimony, or lead salt, the fluorescence is green. Calcium tungstate exhibits no thermoluminescence at room temp. ; but when it is cooled to —192°, exposed to X-rays, and its temp. allowed to rise, it becomes luminescent, the glow is then extinguished, and as the temp. still continues to rise, a second luminescence appears. A small amount—say 0·1 grm.—shows only one thermoluminescence. The luminescence of calcium tungstate in cathode rays resembles that produced by X-rays. J. O. Perrine studied the ultra-violet spectrum excited by X-rays ; F. E. Swindells, and K. Becker and H. Becker-Rose, the fluorescence in the X-rays. W. Jander gave for the electrical conductivities, $11{\cdot}6\times10^{-6}$, $3{\cdot}2\times10^{-6}$, and $1{\cdot}3\times10^{-6}$, respectively at 1157°, 1072°, and 994°.

A. Radiguet used scheelite in making fluorescent screens for X-rays ; and M. G. Bogoslovsky and co-workers recommended adding 0·01 to 0·5 per cent. of tin oxide to calcium tungstate used for fluorescent screens ; and A. Schleede and T. H. Tsao showed that when commercial tungstic acid or ammonium tungstate is purified by alternate treatment with conc. hydrochloric acid, or aqua regia, and soda-lye or aq. ammonia, and then converted into calcium tungstate by treatment with calcium chloride and ignition at 1000°, the X-ray fluorescence is about equal to that of the best technical specimens, whilst phosphorescence is sometimes present, sometimes absent. The latter property is inhibited by addition of calcium molybdate, but the fluorescence is sensibly diminished. Similar preparations are obtained from ammonium tungstate and calcium chloride in very dil. soln. Calcium tungstate, prepared from repeatedly crystallized sodium tungstate and calcium chloride, still exhibited phosphorescence, but a non-phosphorescent material resulted when recrystallized ammonium tungstate was used as initial material. The residues obtained from the mother-liquors from the ammonium tungstate contained arsenic and molybdenum. The addition of ammonium arsenate to ammonium tungstate, previous to precipitation with calcium chloride, leads to preparations with good fluorescence but marked phosphorescence ; similar results are induced by ammonium antimonate. Ammonium molybdate does not induce phosphorescence. H. Hirschi, and K. Endell observed the luminescence of scheelite when the mineral is exposed to radium rays ; and A. Pochettino, when it is exposed to cathode rays. F. C. Henrici and J. F. L. Hausmann, and T. A. L. du Moncel said that scheelite is a conductor, and E. Wartmann, and F. Beijerinck, that it is a non-conductor of electricity. E. E. Fairbanks gave 7·7 (water 81) for the dielectric constant of scheelite ; and H. Saegusa studied this subject.

E. F. Anthon obtained normal **strontium tungstate,** $SrWO_4$, by mixing soln. of a strontium salt with normal potassium or sodium tungstate ; or by boiling freshly-precipitated strontium carbonate with tungstic acid and water. J. Lefort used soln. of strontium acetate and normal sodium tungstate. H. Schultze, and E. Zettnow prepared the crystals of the salt by melting mixtures of sodium tungstate, strontium chloride, and sodium chloride. L. Michel recommended an excess of the flux—sodium chloride. G. Tammann observed that when strontium carbonate is heated with tungsten trioxide, carbon dioxide is expelled, and strontium tungstate is formed. Strontium tungstate appears as a white, amorphous powder ; and A. Cossa described the crystals as tetragonal bipyramids with the axial ratio $a : c = 1 : 1·5582$. E. K. Broch calculated from the X-radiogram the space-lattice with $a = 5·405$ A., $c = 11·90$ A., $a : c = 1 : 2·202$; and density, 6·372. F. Zambonini gave 6·184 for the sp. gr. F. A. Henglein gave 54·27 for the mol. vol. When the voluminous powder is heated to redness, it becomes incandescent, and is afterwards compact. It remains white after being heated to redness. G. Tammann gave 56·4 Cals. for the heat of formation per mol. W. Jander gave for the electrical conductivities 107×10^{-6}, $62·5 \times 10^{-6}$, and $5·8 \times 10^{-6}$ respectively at 1040°, 900°, and 733°. E. F. Anthon said that strontium tungstate is insoluble in water, but J. Lefort found that 100 parts of water at 15° dissolve 0·14 part. E. F. Anthon found that strontium tungstate is soluble in a boiling soln. of oxalic acid, and, on cooling, the liquid becomes turbid. E. F. Smith and R. H. Bradbury found that the salt is easily decomposed when heated and is not therefore a suitable form in which to precipitate tungsten for analysis.

F. de Carli found that a mixture of barium and tungsten oxides when heated shows a thermal effect at 190° ; and G. Tammann observed that the two oxides unite to form **barium tungstate,** $BaWO_4$, between 300° and 550°. The subject was discussed by W. Jander. J. A. Hedvall and N. von Zweigbergk found that with a mixture of barium dioxide and tungsten trioxide, oxygen begins to come off at 250° ; and the greatest reaction velocity in forming tungstate is between 450° and 525°. The subject was studied by W. Jander, who found that the reaction with barium carbonate begins at 300°. E. F. Anthon, and A. Cossa obtained the salt by mixing soln. of a barium salt and of normal potassium or sodium tungstate, or by boiling barium carbonate with water and tungstic acid. J. Lefort obtained this tungstate by mixing aq. soln. of barium acetate and normal sodium tungstate, the washed product is heated to drive off the combined water. A. Geuther and E. Forsberg, and E. Zettnow obtained crystals of the salt by melting a mixture of normal sodium tungstate, barium chloride, and sodium chloride, slowly cooling the liquid, and washing out the soluble matters with water. L. Michel recommended using an excess of sodium chloride as a flux. A. Cossa found that the white, tetragonal, bipyramidal crystals have the axial ratio $a:c=1:1·6046$. I. I. Navano and J. Palacios' X-radiograms of this salt indicated the existence of 4 mols. in the elementary parallelopipedal cell. L. Vegard and A. Refsum gave $a=7·908$ A., $c=12·689$ A., $a:c=1:1·605$; the radius of the oxygen atom is 1·24; of the metal in WO_4, 1·03; and of the positive ion, 1·21 A. F. Zambonini gave 6·35 for the sp. gr., and F. W. Clarke and J. L. Davis, 5·0422 at 15°. F. A. Henglein gave 60·69 for the mol. vol. E. Zettnow found that the salt fuses with difficulty, and becomes incandescent at a red-heat. G. Tammann gave 73·5 Cals. for the heat of formation per mol.; J. A. Hevdall and N. von Zweigbergk gave 80 Cals. For the luminescence when exposed to X-rays, *vide supra*, calcium tungstate. W. Jander obtained for the electrical conductivity, $36·6\times10^{-6}$, $6·9\times10^{-6}$, and $1·8\times10^{-6}$ respectively at 1123°, 994°, and 815°. The salt is not changed by exposure to air, and J. Lefort found it to be sparingly soluble in water. E. F. Smith and R. H. Bradbury said that it is more soluble in ammonium nitrate soln. than it is in water; and that the salt is a suitable form in which to precipitate tungsten for analysis. E. Zettnow said that the salt is decomposed by fusion with sodium carbonate, and A. Geuther and E. Forsberg, by boiling it with nitric acid. C. Scheibler reported octahedral crystals of the *hemihydrate*, $BaWO_4.\frac{1}{2}H_2O$, to be formed when the mother-liquor obtained in the preparation of sodium barium tungstate is treated with baryta-water, and the precipitate filtered and washed; it is also formed by treating a soln. of barium metatungstate, or of metatungstic acid with baryta-water. E. Péchard reported the *dihydrate*, $BaWO_4.2H_2O$, to be formed by the action of an eq. of metatungstic acid on baryta water; he also obtained a *tetrahydrate*, $BaWO_4.4H_2O$, in a similar manner. E. Zettnow obtained a *hemipentahydrate*, $BaWO_4.2\frac{1}{2}H_2O$, by adding barium chloride to a soln. obtained by boiling sodium dodecatungstate with acetic acid and hydrochloric acid as long as precipitation occurs. The amorphous, voluminous precipitate is washed by decantation, and dried at 30° to 40°. L. Kahlenberg and W. J. Trautmann found that silicon reacts with difficulty with barium tungstate, yielding a slag and a few small globules of what is probably a silicide.

C. Scheibler reported a **beryllium tungstate** to be formed by crystallization from a syrupy soln. G. Tammann observed no singular point on the heating curve obtained from a mixture of beryllium oxide and tungsten trioxide. F. de Carli obtained no singular point on the heating curve of mixtures of magnesia and tungsten trioxide, but G. Tammann observed that **magnesium tungstate,** $MgWO_4$, is formed between 300° and 600°, and this is shown by a hump on the heating curve. A. Geuther and E. Forsberg obtained the anhydrous salt by a mixture of sodium tungstate, magnesium chloride, and sodium chloride. L. Michel recommended an excess of sodium chloride. The crystals were also prepared by N. S. Manross, and V. M. Goldschmidt. Octahedral and columnar crystals can be isolated by washing the product. The crystals were examined by F. Machatschky, and V. M. Goldschmidt. The monoclinic prisms have the axial ratios $a:b:c=0·8263:1:0·8703$, and $\beta=89°\ 40'$. From the X-radiograms, E. K. Broch found $a:b:c=4·67:5·66:4·92$, and $\beta=89°\ 35'$, or $a:b:c=0·828:1:0·871$—F. Machatschky gave $0·8263:1:0·8703$, and $\beta=89°\ 40'$. The monoclinic crystals have two $MgWO_4$ mols. per unit cell, and the sp. gr. is 5·66. The crystals are decomposed when heated with nitric acid. F. Ullik said that the salt does not melt at a bright red-heat. G. Tammann gave 3·4 Cals. for the heat of formation per mol from its constituent oxides. W. Jander obtained about $0·02\times10^{-6}$ for the electrical conductivity of the salt at 800°; and he obtained values for the diffusion coeff. J. Lefort reported a *trihydrate*, $MgWO_4.3H_2O$, to be formed by mixing soln. of normal sodium tungstate and magnesium acetate in eq. proportions in the presence of alcohol. The white, amorphous powder remains white when gradually heated; it is very soluble in water, and almost insoluble in alcohol. The aq. soln. forms a syrup when evaporated, but does not crystallize. F. Ullik obtained a *heptahydrate*, $MgWO_4.7H_2O$, by boiling tungstic acid and magnesium carbonate suspended in water. The clear, filtered soln. on cooling deposits lustrous prisms which dissolve a little in cold water, but freely in hot water. They lose water when heated. F. Rodolico obtained a complex $MgWO_4.X.10H_2O$ with hexamethylenetetramine. According to F. Ullik, if a conc. aq. soln. of the heptahydrate be mixed with a soln. of potassium tungstate, a white precipitate of **potassium magnesium tungstate** of variable composition is formed. If a soln. of eq. proportions of the two salts be evaporated, the product also has a variable composition, although on one occasion the composition approximated $K_2WO_4.MgWO_4.2H_2O$.

A. Geuther and E. Forsberg melted a mixture of sodium tungstate, zinc chloride, and sodium chloride, and leached the product with boiling water; there remained colourless crystals of **zinc tungstate,** $ZnWO_4$, considered to be isomorphous with calcium tungstate. E. Zettnow, and L. Michel also prepared the salt and supposed it to furnish rhombic crystals. E. K. Broch observed that the crystals are monoclinic like those of the magnesium salt. L. A. Hallopeau also obtained this salt by heating a mixture of sodium paratungstate and powdered zinc, and washing the cold product with water. E. K. Broch found that the X-radiograms corresponded with a space-lattice having $a=4·68$ A., $b=5·73$ A., $c=4·95$, and $\beta=89° 30'$, with the axial ratios $a:b:c=0·817:1:0·864$, and the calculated density 7·79. For the luminescence of zinc tungstate, *vide supra,* calcium tungstate. J. Lefort found that the *hydrate,* $ZnWO_4.H_2O$, is formed by double decomposition as in the case of calcium tungstate, and he added that the product is slightly soluble in water. W. Jander obtained $8·5\times10^{-6}$ for the electrical conductivity at 1000°, and $1·1\times10^{-6}$ at 850°; and he also calculated values for the diffusion coeff. S. H. C. Briggs obtained **zinc tetramminotungstate,** $ZnWO_4.4NH_3.3H_2O$, as in the case of the copper salt, by allowing a mixture of an ammoniacal soln. of zinc and ammonium tungstates gradually to diffuse into alcohol. The tetrahedral crystals gradually give off ammonia at ordinary temp. F. de Carli found that when a mixture of cadmium oxide and tungsten trioxide is heated, evidence of combination occurs at 250°; and W. Jander studied the action of solid cadmium and magnesium oxides on solid zinc tungstate, $MgO+ZnWO_4=ZnO+MgWO_4$, etc. A. Geuther and E. Forsberg, and L. Michel obtained **cadmium tungstate,** $CdWO_4$, by the method employed for the zinc salt. E. Zettnow also obtained the salt by a similar process, and described the product as a canary-yellow powder consisting of rhombic octahedra. E. F. Anthon obtained the *dihydrate,* $CdWO_4.2H_2O$, as a white powder, by treating a soln. of a cadmium salt with sodium or potassium tungstate. It loses its water when heated, and it is soluble in phosphoric, and oxalic acids, and in aq. ammonia, but not in water. E. F. Smith and R. H. Bradbury said that after the tungstate has been heated it is not soluble in acids; and they found the salt a suitable form in which to precipitate tungstates for the quantitative determination of tungsten. W. Jander obtained for the electrical conductivity of the cadmium salt 202×10^{-6}, $64·5\times10^{-6}$, and $2·8\times10^{-6}$ respectively at 1043°, 942°, and 761°. W. Jander studied the reaction: $MgO+CdWO_4=CdO+MgWO_4$. J. R. Partington discussed the fluorescence and phosphorescence of the salt. W. Jander studied the action of magnesium oxide on solid cadmium tungstate.

E. F. Anthon obtained **mercurous tungstate,** Hg_2WO_4, as a yellow precipitate by mixing a soln. of mercurous nitrate and sodium tungstate. When dried, it is dark yellow, and after calcination, tungsten trioxide remains. J. J. Berzelius examined the salt as a means of quantitatively determining tungsten. E. F. Anthon added that the yellow salt appears at first tasteless, but after a time it has a weak, metallic taste. J. Lefort found that **mercuric tungstate,** $HgWO_4$, is precipitated by adding a neutral soln. of mercuric acetate to a sat. soln. of sodium tungstate. The straw-yellow product becomes lemon-yellow when dried. It is not very stable, and is decomposed when washed for a long time with water; it is sparingly soluble in water. E. F. Anthon found that if ammonium ditungstate and neutral mercuric nitrate soln. be mixed, a white precipitate approximating **ammonium mercuric tungstate,** $(NH_4)_2WO_4.HgWO_4.H_2O$, is formed. It can be dried at 100°, but at

200°–250° it gives off water and ammonia, leaving a mixture of mercuric and tungsten oxides. It is insoluble in water, and is decomposed by alkali-lye, and acids.

The *borotungstates* were discussed in connection with the borates—**5.** 32, 15. G. Tammann [6] observed that when a mixture of alumina and tungsten trioxide is heated, no evidence of the formation of a compound is shown on the heating curve; but F. A. Bernoulli heated a mixture of a mol of alumina with 3 mols of tungsten trioxide in a porcelain oven for 18 hrs. and obtained a crystalline mass, presumably **aluminium tungstate,** $Al_2O_3.3WO_3$, or $Al_2(WO_4)_3$. E. F. Anthon obtained a precipitate of the hydrate by adding sodium tungstate to a soln. of an aluminium salt. W. Lotz found that the precipitate is insoluble in water, and in a soln. of sodium tungstate, but it is soluble in aq. ammonia, and in soln. of alum, sodium hydroxide, and phosphoric and oxalic acids. J. Lefort said that when a soln. of alum is poured into a soln. of normal sodium tungstate, the *octohydrate*, $Al_2(WO_4)_3.8H_2O$, is precipitated as a white, voluminous mass. 100 parts of water at 15° dissolve 0·0667 part of the octohydrate. Complex aluminophosphatotungstates, aluminoarsenatotungstates, and aluminoantimonatotungstates have been prepared; and also complex **aluminotungstates.** Thus, by boiling a mixture of aluminium hydroxide and a soln. of ammonium paratungstate, C. W. Balke and E. F. Smith obtained **ammonium aluminotungstate,** $3(NH_4)_2O.Al_2O_3.9WO_3.4H_2O$, as a dense, highly refractive syrup, which, on drying, leaves a translucent mass. The dry, powdered salt dissolved in conc. nitric acid; precipitation did not occur, even upon boiling. The salt was soluble also in conc. hydrochloric acid without the production, in the cold, of a precipitate, but when the soln. was vigorously boiled a yellow-coloured precipitate separated. Mercurous nitrate produced, in its aq. soln., a yellowish-white-coloured precipitate. The precipitate caused by barium chloride was almost insoluble in hot water. After drying, acids failed to dissolve it. In a slightly ammoniacal soln. of the salt, silver nitrate produced a yellowish-white precipitate, soluble in a large vol. of hot water. L. C. Daniels prepared **copper aluminotungstate,** $2CuO.Al_2O_3.9WO_3.16\frac{1}{2}H_2O$, by adding a conc. soln. of ammonium aluminotungstate to a 10 per cent. soln. of copper sulphate; or to an ammoniacal soln. of cupric hydroxide. C. W. Balke and E. F. Smith added silver nitrate to an ammoniacal soln. of ammonium aluminotungstate, and obtained a yellowish-white precipitate of **ammonium silver aluminotungstate,** $11Ag_2O.21(NH_4)_2O.4Al_2O_3.36WO_3$. The precipitate obtained by adding barium chloride to a soln. of ammonium aluminotungstate was found by L. C. Daniels to be **barium aluminotungstate,** $8BaO.Al_2O_3.9WO_3.7H_2O$; while a soln. of zinc oxide in aq. ammonia gives a white precipitate of **zinc aluminotungstate,** $ZnO.Al_2O_3.9WO_3.20H_2O$; and with mercurous nitrate, a pale yellow flocculent precipitate of **mercurous aluminotungstate,** $5Hg_2O.Al_2O_3.9WO_3$, was formed. A. Rogers and E. F. Smith treated a soln. of ammonium aluminotungstate with mercurous nitrate and obtained a yellowish-white precipitate supposed to be an **ammonium mercurous aluminotungstate.**

C. Renz [7] obtained **indium tungstate,** $In_2(WO_4)_3.8H_2O$, by adding a soln. of sodium tungstate to one of an indium salt. The white precipitate dries to a horny mass. H. Flemming obtained **thallous tungstate,** Tl_2WO_4, by mixing soln. of normal sodium tungstate and a thallous salt; or by boiling tungstic acid and thallous carbonate. The precipitate consists of microscopic, highly refracting, six-sided plates. P. S. Oettinger added that the precipitate is insoluble in water, sparingly soluble in aq. ammonia, but is soluble in hot soln. of alkali hydroxide or carbonate. E. Schaefer could not prepare normal thallous tungstate; **thallic tungstate** has not been reported.

G. Tammann [8] observed evidence of the formation of **cerous tungstate,** $Ce_2(WO_4)_3$, when a mixture of ceric oxide and tungsten trioxide is heated. The heating curve shows that an endothermic reaction occurs between 240° and 600°. According to A. Cossa and M. Zecchini, when a soln. of cerous sulphate is poured into one of sodium tungstate, an amorphous, pale yellow precipitate of cerous tungstate is formed. After heating to redness, the amorphous precipitate becomes crystalline. F. R. M. Hitchcock found that a soln. of sodium tungstate gives a precipitate with soln. of cerium salts, the precipitation is not complete, and the addition of alcohol precipitates other cerium salts along with the cerium tungstate in soln.

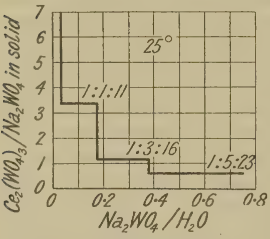


Fig. 41.—Equilibrium in the System : $Ce_2(WO_4)_3$–Na_2WO_4–H_2O.

P. Didier found that if ceric oxide be added in small portions at a time to fused sodium paratungstate, kept in excess, minute, yellow octahedra of normal cerous tungstate, resembling the crystals of scheelite, are formed. Larger crystals are produced by fusing precipitated cerous tungstate with sodium chloride out of contact with air. H. Traube obtained crystals of cerium tungstate as a sublimate by heating to a high temp. a mixture of the tungstate with sodium and potassium chlorides. F. Zambonini gave for the axial ratio of the crystals $a : c = 1 : 1{\cdot}5257$, and he examined the optical constants of isomorphous mixtures with cerous tungstate. F. Zambonini found the sp. gr. of $Ce_2(WO_4)_3$ to be 6·77 at 16·5°, and the mol. vol. 151·3. A. Cossa and M. Zecchini gave for the sp. gr. 6·514 at 12°; and for the sp. ht., 0·0821. F. Zambonini gave 1089° for the m.p. A. Rogers and E. F. Smith prepared **ammonium cerous tungstate,** $2(NH_4)_2O.Ce_2O_3.16WO_3.2H_2O$, as a red, transparent glass, insoluble in water, by boiling cerium hydroxide for 8 hrs. with a soln. of ammonium paratungstate, filtering the mixture, and evaporating it to dryness. By dissolving cerium oxide and tungsten trioxide in a fused mixture of sodium tungstate and chloride, A. J. Högbom obtained crystals of **sodium cerous tungstate,** $Na_8Ce_2(WO_4)_7$. P. Didier also obtained a complex tungstate, $Na_2Ce_2(WO_4)_4$, in sulphur-yellow, octahedral crystals, by dissolving precipitated cerous tungstate in normal sodium tungstate. G. Carobbi and G. Tancredi found that three crystalline compounds can exist in the system $Ce_2(WO_4)_3$–Na_2WO_4–H_2O, at 25°. The results are summarized in Fig. 41. These are $Ce_2(WO_4)_3.Na_2WO_4.11H_2O$; $Ce_2(WO_4)_3.3Na_2WO_4.16H_2O$; and $Ce_2(WO_4)_3.5Na_2WO_4.23H_2O$. They are stable in air; and since the velocity curve of the dehydration of the salts over sulphuric acid, or calcium chloride shows breaks, other hydrates probably exist. Thus with sulphuric acid of sp. gr. 1·58, at 25°, for the 1 : 1 : 11-salt:

Time . .	1·25	4·25	8·33	23·0	38·0	113·7	756·7	4000 min.
Loss . .	3·83	4·92	5·78	6·80	7·09	7·96	8·39	8·39 per cent.

with the 1 : 3 : 16-salt:

Time . .	1·25	4·25	8·33	23·0	66·0	139·7	782·7	3991 min.
Loss . .	3·13	5·22	5·95	7·30	7·86	9·71	9·99	9·99 per cent.

and with the 1 : 5 : 23-salt:

Time . .	1·25	4·92	8·33	23·0	66·0	139·8	783·0	3991 min.
Loss . .	3·49	5·06	5·93	7·07	7·77	8·46	9·95	9·95 per cent.

According to F. R. M. Hitchcock, a soln. of sodium tungstate added to one of lanthanum chloride, in the presence of alcohol, gives a precipitate, presumably **lanthanum tungstate,** which, on drying has a delicate blue colour. H. Traube obtained crystals as a sublimate by the method indicated in connection with cerium tungstate. A. Rogers and E. F. Smith prepared **ammonium lanthanum tungstate,** $2(NH_4)_2O.La_2O_3.16WO_3.16H_2O$, as in the case of the corresponding cerium salt. It is white, and insoluble. A. J. Högbom dissolved lanthanum oxide and tungsten trioxide in a fused mixture of sodium chloride and an excess of sodium tungstate, and obtained crystals of **sodium lanthanum tungstate,** $Na_8La_2(WO_4)_7$; if the sodium chloride be in excess, crystals of $Na_6La_4(WO_4)_9$ are formed. A. Rogers and

E. F. Smith observed that when a dil. soln. of ammonium lanthanum tungstate is treated with silver nitrate, white, insoluble **silver lanthanum tungstate,** $5Ag_2O.La_2O_3.16WO_3.4H_2O$, is formed; and with barium chloride, white and insoluble **barium lanthanum tungstate,** $5BaO.La_2O_3.16WO_3.16H_2O$, is produced. F. R. M. Hitchcock prepared **præseodymium tungstate** as a greenish-yellow gelatinous precipitate on treating a soln. of sodium tungstate with a soln. of præseodymium chloride; and **neodymium tungstate** was obtained in a similar way as a pale rose-coloured precipitate which becomes violet after ignition. A. Rogers and E. F. Smith prepared **ammonium præseodymium tungstate,** $2(NH_4)_2O.Pr_2O_3.16WO_3.16H_2O$, as in the case of the corresponding cerium salt. It appears as a green, transparent, gummy mass which is sparingly soluble in water. A pink-coloured salt, $3(NH_4)_2O.Nd_2O_3.16WO_3.20H_2O$, was obtained in a similar way. By treating the ammonium salt with silver nitrate, greenish-white **silver præseodymium tungstate,** $4Ag_2O.Pr_2O_3.16WO_3.8H_2O$, was prepared; and with barium chloride, white **barium præseodymium tungstate,** $4BaO.Pr_2O_3.16WO_3.7H_2O$, as well as $6BaO.Pr_2O_3.16WO_3.9H_2O$, were obtained. Pink and insoluble **barium neodymium tungstate,** $6BaO.Nd_2O_3.16WO_3.17H_2O$, was also prepared by adding barium chloride to a soln. of the ammonium salt. H. Traube obtained crystals of **didymium tungstate,** $Di_2(WO_4)_3$, as a sublimate as in the case of cerium tungstate. The salt was prepared by A. Cossa, who gave 6·69 for the sp. gr. at 14°. A. J. Högbom also reported **sodium didymium tungstate,** $Na_6Di_4(WO_4)_9$, by dissolving the oxide in a fused mixture of sodium tungstate and chloride with the tungstate in excess—if the chloride is in excess, $Na_2O.Di_2O_3.4WO_3$ is formed. When barium metatungstate is treated with the theoretical quantity of samarium sulphate, and the soln. evaporated over conc. sulphuric acid, topaz-yellow crystals of **samarium tungstate,** $Sa_2O_3.12WO_3.35H_2O$, were formed—*vide infra*, the metatungstates; they become opaque when exposed to light. The sp. gr. is 3·992 to 3·996 at 18·4°. The salt is not deliquescent, and is freely soluble in water. A. J. Högbom prepared **sodium samarium tungstate,** $Na_6Sa_4(WO_4)_9$, from a soln. of samarium oxide in a fused mixture of sodium tungstate and an excess of sodium chloride; similarly with **sodium gadolinium tungstate,** $Na_6Gd_4(WO_4)_9$, using an excess of sodium tungstate; with **sodium erbium tungstate,** $Na_6Er_4(WO_4)_9$, using an excess of sodium chloride; and with **sodium yttrium tungstate,** $Na_8Y_2(WO_4)_7$, using an excess of sodium tungstate. By treating barium metatungstate with ytterbium sulphate, and concentrating the soln., A. Cleve obtained **ytterbium tungstate,** $Yb_2O_3.12WO_4.35H_2O$, in prismatic crystals, not deliquescent, stable in air, and freely soluble in water; and by fusing a mixture of ytterbium oxide and sodium tungstate and chloride, extracting the mass with water, the residue contains a pale reddish-grey, microcrystalline powder of **ytterbium oxytungstate,** $Yb_2O_3.WO_3$, or $(YbO)_2WO_4$; and colourless, acicular crystals of **sodium ytterbium tungstate,** $4Na_2O.2Yb_2O_3.7WO_3$, which can be separated by evaporation. If fused with sodium chloride as flux, microscopic needles of insoluble $9Na_2O.Yb_2O_3.12WO_3$ appear to be formed.

The **silicotungstates** were discussed in connection with the silicates—**6**. 40, 50; and the *titanium tungstates* have not been investigated. O. Kulka[9] reported that if a soln. of zirconium nitrate be poured into a cold soln. of ammonium metatungstate, and the gelatinous precipitate be washed by suction with hot water, and dried, the product has the composition **zirconium tungstate,** $5ZrO_2.9WO_3.33H_2O$; if sodium paratungstate be employed, the dried precipitate has the composition $5ZrO_2.7WO_3.21H_2O$. Both products are insoluble in water; the first is insoluble and the second is soluble in hydrochloric acid. Both may be mixtures. L. A. Hallopeau reported **ammonium zirconium tungstate,** $3(NH_4)_2O.ZrO_2.10WO_3.14H_2O$, to be formed by crystallization in vacuo from a syrupy soln. of zirconium hydroxide in ammonium paratungstate. The small prismatic crystals act strongly on polarized light and show parallel extinction. They lose water even in contact with the mother-liquor. The salt is freely soluble in water, and is very deliquescent. O. Kulka said that soln. of normal sodium tungstate, and of sodium or ammonium metatungstate, do not dissolve zirconium hydroxide. O. Kulka reported **potassium zirconium tungstate,** $K_2O.ZrO_2.2WO_3.33H_2O$, to be formed by boiling a soln. of potassium paratungstate with zirconium hydroxide, after separating the excess of paratungstate. He represented the constitution $KO.WO_2.O.ZrO.O.WO_2.OK$. L. A. Hallopeau found that a boiling soln. of potassium paratungstate dissolves zirconium hydroxide, and the soln. deposits small crystals of the composition $4K_2O.ZrO_2.10WO_3.15H_2O$, and which act feebly on polarized light. When the mother-liquor is concentrated in vacuo, it furnishes small prismatic crystals of the composition $4K_2O.2ZrO_2.10WO_3.20H_2O$, which act strongly on polarized light, and show extinction at 30° from the axis of elongation. Both these compounds are almost insoluble in cold water, are converted into insoluble compounds when heated, and yield a mixture of tungstate and zirconate when fused with alkali carbonates. In general properties, they resemble the silicotungstates; the zirconodecatungstate is analogous in composition to the silicodecatungstate, except that it contains a somewhat smaller proportion of water. According to J. J. Berzelius, a soln. of a thorium salt gives a white, flocculent precipitate of **thorium tungstate** when treated with sodium tungstate; and, according to W. Nernst, if a mol of thoria is heated with 2 mols of tungsten trioxide a thorium tungstate is formed. A. J. Högbom prepared microscopic, tetragonal crystals of **sodium thorium tungstate,** $Na_4Th(WO_4)_4$, by dissolving thoria in a fused mixture of sodium chloride and an excess of sodium tungstate. G. N. Wyrouboff said that thoria readily dissolves in many acid tungstates forming salts of complex acids.

According to F. de Carli,[10] when a mixture of stannous oxide and tungsten trioxide is heated, combination begins at about 265°. E. F. Anthon observed that **stannous tungstate,** $SnWO_4.6H_2O$, is formed as a yellow powder by mixing soln. of sodium tungstate and stannous chloride. Hydrochloric acid extracts the stannous oxide, and the tungsten trioxide is at the same time reduced to the blue oxide. The salt is insoluble in water, slowly soluble in phosphoric acid, and soluble in oxalic acid, and potash-lye. W. Lotz found that on mixing soln. of ammonium paratungstate and ammonium chlorostannate, a white flocculent precipitate, presumably stannic tungstate, $9SnO_2.13WO_3.nH_2O$, is formed. It is soluble in an excess of the chlorostannate, but not in a soln. of ammonium tungstate. It is soluble in phosphoric, oxalic, and tartaric acids. S. Prakash and N. R. Dhar found that the viscosities of a soln. of **stannic tungstate,** $Sn(WO_4)_2.nH_2O$, having 8 c.c. of $1{\cdot}35M$-$SnCl_4$, 2 c.c. of water, and 14 c.c. of a 15 per cent. soln. of sodium tungstate, at 30°, are:

Age . .	0	90	125	168	210	245	283 min.
Viscosity .	0·01349	0·01570	0·01640	0·01691	0·01807	0·02015	0·02280

The soln. sets to a firm, white jelly in 10 hrs. G. von Knorre treated a molten mixture of a mol of lithium oxide and 2 mols of tungsten trioxide with tin, and obtained, presumably, **lithium stannic tungstate,** $2Li_2O.SnO_2.6WO_3$, as a steel-grey, amorphous powder.

A. Breithaupt,[11] described a mineral which he called *Scheelbleispath* occurring at Zinnwald, Bohemia, and at Bleiberg, Carinthia. F. S. Beudant called it *Scheelitine;* and W. Haidinger, **stolzite**—after Dr. Stolz of Teplitz who first drew attention to the mineral. The same mineral occurs in Coquimbo, Chili; at Southampton, and Loudville, Massachusetts; Marianna de Itacolumi, Brazil; Bena e Padru, Sardinia; and the Broken Hill Mines, New South Wales. Analyses of the mineral by W. A. Lampadius, K. H. T. Kerndt, W. Florence, C. Hlawatsch, and of artificial **lead tungstate,** $PbWO_4$, by E. F. Anthon, H. C. Germs, N. S. Manross, and C. Friedheim are in agreement. E. J. Chapman obtained a variety from Coquimbo containing 6·37 per cent. of calcium, $(Ca,Pb)WO_4$. Another mineral called **raspite**—after Mr. Rasp, the discoverer of the Broken Hill Mines—was described by C. Hlawatsch. It occurs at the Broken Hill Mines, N.S.W., and is also a normal lead tungstate, or possibly $Pb_2(WO_4)_3$—but stolzite occurs in tetragonal crystals, raspite in monoclinic crystals. A mixed molybdate and tungstate, $Pb(W,Mo)O_4$, between stolzite and wulfenite from Chillagoe, Queensland, was called **chillagite** by A. T. Ullmann, and C. D. Smith and L. A. Cotton. J. C. H. Mingaye reported some analyses. F. Krantz called it *lyonite* or *lionite* after D. Lyon.

F. de Carli said that mixtures of lead oxide and tungsten trioxide begin to react at 210°; G. Tammann observed a hump on the heating curve between 480° and 700°; and D. Balareff said that the maximum effect occurs at about 700°. W. Jander said that the reaction with lead oxide and tungsten trioxide begins at 480°. E. F. Anthon, J. Brown, and E. F. Smith and R. H. Bradbury obtained lead tungstate as a white, flocculent precipitate by treating a soln. of a lead salt with a soln. of potassium tungstate; C. Friedheim mixed lead acetate and metatungstic acid in dil. soln.; F. M. Jäger and H. C. Germs treated with lead acetate a soln. of sodium tungstate, or a boiling, ammoniacal soln. of tungstic acid mixed with acetic acid. W. Lotz mixed hot conc. soln. of lead acetate or nitrate and ammonium metatungstate, and on cooling, found that the liquid solidified to a crystal magma, which was soluble in much water, and from this soln., on spontaneous evaporation, crystals of lead metatungstate were formed. E. F. Smith filtered a soln. of the crystal magma at room temp., and evaporated it on an iron plate over a small flame. As the liquid became hot, it became turbid and finally deposited a dense, white, insoluble powder. This white powder had a composition of the *hemipentahydrate*, $PbWO_4.2\frac{1}{2}H_2O$. N. S. Manross, and W. Meyerhoffer melted a mixture of sodium tungstate and lead chloride; and L. Michel, a mixture of sodium tungstate, lead chloride, and sodium chloride in a crucible lined with magnesia. The cold product was lixiviated with water. L. Michel also used lead sulphate in place of the chloride. The crystals formed by the fusion processes correspond with those of stolzite. E. Zettnow found that amorphous lead tungstate becomes crystalline when fused with sodium tungstate; and H. Traube that lead tungstate may be obtained as a crystalline sublimate by heating it mixed with sodium and potassium chlorides, to a high temp.

The mineral stolzite occurs in green, yellowish-grey, brown, and red masses of crystals indistinctly aggregated. The artificial preparation is colourless. According to K. H. T. Kerndt, the crystals are tetragonal with pyramidal hemihedrism. The axial ratio $a:c=1:1{\cdot}5667$; C. Hlawatsch gave $1:1{\cdot}5606$. The habit is acute octahedral, and the crystals may form plates or pyramids. The (001)- and (111)-changes are imperfect. C. Hlawatsch, and W. Florence examined the corrosion figures. The optical character is negative. The crystals of stolzite were described by A. Lévy, F. von Kobell, B. K. Emerson, E. Artini, D. Lovisato, E. Hussak, F. C. Naumann, etc. C. Hlawatsch observed that raspite forms monoclinic prisms with the axial ratios $a:b:c=1{\cdot}3363:1:1{\cdot}1112$, and $\beta=107°\ 41'$; and with another specimen $1{\cdot}34497:1:1{\cdot}11468$, and $\beta=72°\ 23'$. The (100)-cleavage is complete. According to E. S. Larsen, the optic axial angle 2V is nearly zero; and the optical character is positive. L. Vegard and A. Refsum found that the X-radiograms corresponded with the lattice parameters $a=7{\cdot}696$ A., $c=12{\cdot}010$ A., $a:c=1{\cdot}1561$; a radius of the oxygen atom 1·18 A., of the metal in WO_4, 1·04 A., and of the positive ion, 1·17 A. The sp. gr. of raspite has not been reported; that of stolzite given by K. H. T. Kerndt is 8·1032 to 8·1275; and for artificial lead tungstate, N. S. Manross gave 8·232 to 8·238. P. Niggli gave 8·30 for the sp. gr. of stolzite; and 54·8 for the eq. vol.; J. J. Saslawsky gave 7·9 to 8·1 for the sp. gr., and calculated that a contraction of 0·66 to 0·67 occurs in the formation of lead tungstate from its elements. F. A. Henglein gave 54·81 for the mol. vol. The hardness of stolzite is 2·75 to 3·0; and that of raspite is 2·5 to 3·0. E. Cane found the sp. ht. to be 0·077. F. Zambonini gave 1125° for the m.p. of lead tungstate; and F. M. Jäger and H. C. Germs, 1123°. The latent heat of fusion is said to be smaller than that of lead molybdate. D. Vorländer and H. Hempel observed no sign of a transition temp., but F. M. Jäger and H. C. Germs found that on cooling, there is a transition corresponding with the passage of what they call β-lead tungstate to α-lead tungstate, the form stable at ordinary temp. There is only a small thermal change at the transition temp. The transformation is more marked in the presence of lead sulphate, and it vanishes in the presence of lead chromate and molybdate. In the system: $PbSO_4$–$PbWO_4$, Fig. 42, the solid soln. containing β-$PbWO_4$ separating at the eutectic temp. contains respectively 37 molar per cent. of sulphate, and 7 of the tungstate. The eutectic is at 995° corresponding with 51 molar per cent. of tungstate. The change α-$PbSO_4 \rightleftharpoons \beta$-$PbSO_4$ occurs at 875°, and α-$PbWO_4 \rightleftharpoons \beta$-$PbWO_4$ at 859°. The equilibrium diagram of the system: $PbCrO_4$–$PbWO_4$ is incomplete. There is a eutectic at 837°, and the limiting solid soln. on the tungstate side of the diagram contains 41 molar per cent. of chromate. Lead molybdate and tungstate, Fig. 43, form an isodimorphous series of solid soln. with a transition temp. at 1082°. A mixture containing 75 molar per cent. of lead molybdate is in equilibrium at this temp. with both kinds of solid soln. In the system: PbO–$PbWO_4$, Fig. 45, there is one combination, namely, **lead oxytungstate,** or $PbO.PbWO_4$, that is Pb_2WO_5, melting at 889°. This compound shows no transition temp. corresponding with a polymorphous transformation. The transition temp. is 877°. There are eutectics at 722° corresponding with 82·5° molar per cent. PbO, and one at 882° corresponding with 46 molar per cent. PbO. F. Zambonini studied the f.p. of the system $Ce_2(WO_4)_3$–$PbWO_4$, and found for the following percentage proportions of lead tungstate:

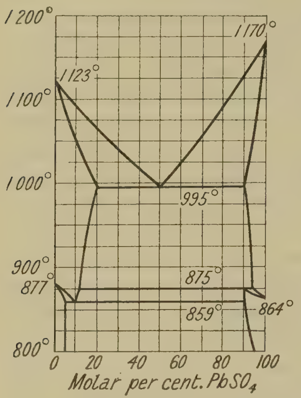


FIG. 42.—Freezing-point Curve $PbSO_4$–$PbWO_4$.

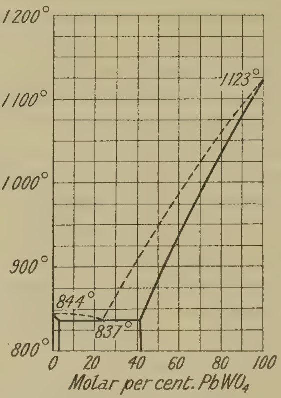


FIG. 43.—Freezing-point Curve $PbCrO_4$–$PbWO_4$.

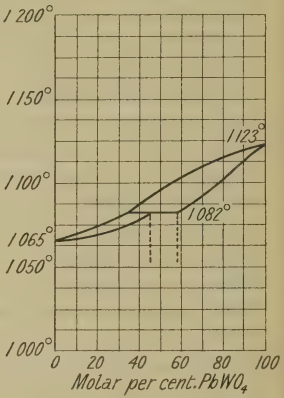


FIG. 44.—Freezing-point Curve $PbMoO_4$–$PbWO_4$.

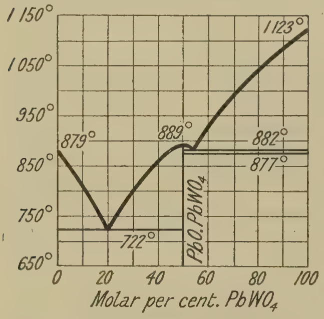


FIG. 45.—Freezing-point Curve of the Mixtures: PbO–$PbWO_4$.

$PbWO_4$ . .	0	20	40	60	80	100 per cent.
F.p. Beginning .	1089°	1103°	1115°	1122°	1123°	1125°
F.p. End . . .	—	1092°	—	1108°	1108°	—

G. Tammann gave for the heat of formation $(PbO,WO_3)=45·4$ Cals. W. Florence found the indices of refraction of stolzite to be $\omega=2·2685$, and $\epsilon=2·182$ for Na-light; and C. Hlawatsch, $\omega=2·2685$, and $\epsilon=2·182$. The index of refraction of raspite approximates 2·6; and E. S. Larsen gave $\alpha=2·27$, $\beta=2·27$, and $\gamma=2·30$. E. Wartmann found stolzite is a non-conductor of electricity. According to

E. F. Anthon, lead tungstate is insoluble in water and in cold nitric acid, but it is soluble in potash-lye. E. F. Smith and R. H. Bradbury said that lead tungstate is insoluble in a soln. of ammonium nitrate, and the presence of this salt facilitates the filtration of lead tungstate from its mother-liquor. L. Kahlenberg and W. J. Trautmann found that silicon reduces lead tungstate with difficulty forming no free metal or silicide.

The *arsenic tungstates* and the arsenato-tungstates have been previously discussed, **9**. 51, 22 ; and the *antimony tungstates*, and the *antimonatotungstates*, **9**. 52, 14. E. F. Smith and R. H. Bradbury[12] obtained insoluble **bismuth tungstate,** presumably $Bi_2(WO_4)_3$, by double decomposition by mixing soln. of sodium tungstate and bismuth nitrate. F. Zambonini found that normal bismuth tungstate is readily obtained by fusing an intimate mixture of bismuth and tungsten trioxides in the theoretical proportions, and allowing the mass to cool slowly. The product contained some monoclinic crystals with the axial ratios $a : b : c = 1{\cdot}006 : 1 : 1{\cdot}520$, and $\beta = 90° \ 34'$. If the monoclinic crystals are heated with an excess of sodium chloride for 3 hrs. at 900° to 1000°, and lixiviated with water, the residue contains tetragonal, bipyramidal crystals with the axial ratio $a : c = 1 : 1{\cdot}566$. The tetragonal crystals correspond perfectly with the tetragonal phase both of the normal molybdates and tungstates of the elements of the yttrium and cerium group, as well as of those of the isomorphogenic elements of the calcium-strontium-barium-lead group, the value of $a : c$ in these compounds varying from $1 : 1{\cdot}542$ to $1 : 1{\cdot}623$. The monoclinic form is distinctly pseudo-tetragonal, the axial ratios differing but little from $1 : 1 : 1{\cdot}566$ and the value of β but little from 90°. This monoclinic form exhibits undeniable crystallographic resemblances to raspite, the monoclinic form of lead tungstate, but the tetragonal bismuth tungstate shows far closer resemblances to stolzite, the tetragonal form of lead tungstate. The sp. gr. of the monoclinic crystals is 8·24 at 7·5°, and the m.p. is 832°. The f.p. curve of the binary system: $PbWO_4$–$Bi_2(WO_4)_3$ is shown in Fig. 46. The curve is characteristic of binary mixtures, either forming no solid soln. or exhibiting extremely limited mutual solubility in the solid state. The crystallization curve first falls rapidly from 1130° to a eutectic point at about 813°, corresponding with about 73 molar per cent. of $Bi_2(WO_4)_3$, and then rises directly to 832°. According to C. W. Balke and E. F. Smith, **ammonium bismuth tungstate,** $3(NH_4)_2O.2Bi_2O_3.11WO_3.10H_2O$, is produced by boiling bismuth hydroxide with a soln. of ammonium paratungstate for about two days, filtering the yellow liquid, and allowing it to cool. The oil of sp. gr. 3·6 which separates dries to a transparent, yellow, vitreous mass. No precipitate was produced on strongly diluting the soln. of this salt with water. Ammonium hydroxide caused no change in its cold dil. soln., but, when the latter was boiled in the presence of ammonia, a copious white precipitate separated. Nitric acid caused no change in the boiling dil. soln. of the salt, but in conc. soln. precipitation occurred on the addition of conc. nitric acid. The addition of a large vol. of hot water again effected soln. Hydrochloric acid occasioned no change in cold or hot dil. soln., while tungstic acid separated on boiling with conc. hydrochloric acid. The corresponding **potassium bismuth tungstate,** $3K_2O.2Bi_2O_3.11WO_3.15H_2O$, forms a yellow oil which dries to a transparent, pale yellow, vitreous mass; and **strontium bismuth tungstate,** $SrO.2Bi_2O_3.11WO_3.11H_2O$, appears as a yellow oil which solidifies to a wax-like mass, and when dried at 100°, forms a hard, yellow, insoluble, vitreous mass. When mercurous nitrate is added to a soln. of the ammonium salt, **mercurous bismuth tungstate** is formed as a yellowish-white precipitate. The complex *vanadatotungstates* have been previously discussed,

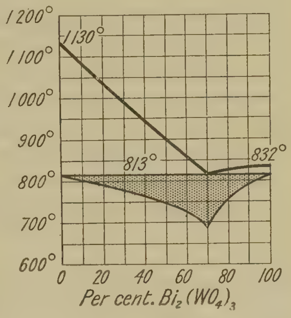


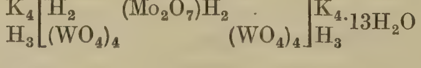
FIG. 46.—Freezing-point Curve of the System: $PbWO_4$–$Bi_2(WO_4)_3$.

9. 54, 14. E. F. Smith[13] found that complex tungstates are formed with columbic and tantalic oxides with tungsten trioxide.

J. Lefort[14] obtained a dark green precipitate of **chromium tungstate,** $Cr_2(WO_4)_3.3H_2O$, by adding a soln. of sodium ditungstate to one of chrome alum; and W. Lotz obtained $Cr_2(WO_4)_3.30H_2O$ from soln. of normal sodium tungstate and chromic chloride. The pale green precipitate is soluble in an excess of the soln. of chromic chloride, and in phosphoric, oxalic, and tartaric acids. It loses 21·27 per cent. or 13 mols. of water when dried over calcium chloride at 100° and 7 more mols., or 12·19 per cent., when calcined at red-heat. The colour is then yellowish-grey. S. Prakash and N. R. Dhar prepared hydrogels of chromic tungstate. J. Lefort obtained **chromium oxytungstate,** $Cr_2O(WO_4)_2.5H_2O$, or $Cr_2O_3.2WO_3.5H_2O$, by pouring a soln. of chromic acetate into a small excess of a soln. of sodium tungstate (1 : 10). The green, pale blue, or violet precipitate dries to a green amorphous powder, which after ignition is brown. 100 parts of water dissolve 0·25 part of the salt at 15°. By mixing very conc. soln. of eq. proportions of chromic acetate and sodium ditungstate, and pouring in alcohol, a dirty green precipitate of **chromium tetratungstate,** $Cr_2O_3.4WO_3.6H_2O$, is formed which furnishes crystalline plates. 100 parts of water at 15° dissolve two parts of the salt. According to W. Kantscheff, a warm mixture of soln. of paratungstate and a chromic salt contain complex chromitungstates. He considers that the different acid tungstates which have been reported are either paratungstates or mixtures of the para- and meta-tungstates.

According to J. J. Berzelius,[15] when ammonium tungstate is mixed with a hydrochloric acid soln. of molybdenum dioxide, a deep purple-red colour appears, from which, if concentrated, ammonium chloride precipitates a red **molybdenum tungstate,** and the mother-liquor retains a pale yellow colour. The precipitate is washed with water containing ammonium chloride, and then with alcohol of sp. gr. 0·87. It is then dried at a gentle heat. The dark purple product is stable in air, and is freely soluble in water. The dil. aq. soln. gradually becomes colourless on exposure to air owing to the formation of a tungstate of molybdenum trioxide. An aq. soln. of the purple-coloured salt is decolorized by ammonia, and it then deposits, on standing, a white, powdered **ammonium molybdenum tungstate** which is insoluble in water, and from which soda-lye separates molybdenum dioxide. Several of the blue oxides of tungsten have been regarded as **tungsten tungstates,** thus, W_5O_{14} can be represented $(W^{V}O)_2.(W^{VI}O_4)_3$, etc.

L. Fernandes neutralized soln. containing stoichiometrical proportions of a molybdate and a tungstate by the addition of acetic acid, followed by crystallization; by the addition of molybdenum to a boiling soln. of a tungstate; and by mixing soln. of a polymolybdate and a polytungstate. There were thus obtained **potassium tetramolybdatoditungstate,** $2K_2O.4MoO_3.2WO_3.12H_2O$, and from the loss of water on heating, the co-ordination formula is taken to be $K_4H_6[H_2(WO_4)_2(MoO_4)_4].8H_2O$, **potassium trimolybdatoditungstate,** $2K_2O.3MoO_3.2WO_3.10H_2O$; **potassium trimolybdatotritungstate,** $3K_2O.3MoO_3.3WO_3.9H_2O$, *enneahydrate* as well as the *trihydrate*; **potassium molybdatopentatungstate,** $3K_2O.MoO_3.5WO_3.5H_2O$; **potassium molybdatotritungstate,** $2K_2O.MoO_3.3WO_3.4H_2O$; **potassium dimolybdatotetratungstate,** $3K_2O.2MoO_3.4WO_3.11H_2O$, or $K_6H_4[H_2(MoO_4)_2(WO_4)_4].8H_2O$; **potassium nickel dimolybdatotetratungstate,** $K_6H_4[Ni(MoO_4)_2(WO_4)_4].nH_2O$, was also prepared; **potassium molybdatodecatungstate,** $5K_2O.MoO_3.10WO_3.12H_2O$; and **potassium molybdatotetratungstate,** $2K_2O.MoO_3.4WO_3.9H_2O$, or



$$\begin{matrix}K_4\\H_3\end{matrix}\left[\begin{matrix}H_2 & (Mo_2O_7)H_2 & \\ (WO_4)_4 & & (WO_4)_4\end{matrix}\right]\begin{matrix}K_4\\H_3\end{matrix}.13H_2O$$

The addition of conc. hydrochloric acid to conc. aq. soln. of these salts results in the precipitation of the free molybdatotungstic acids as white, amorphous powders, and repeated treatment with hydrochloric acid fails to effect a separation of the two acids. Barium salts give white, sparingly soluble, microcrystalline precipitates when added to soln. of the molybdatotungstates ; and by the addition of a soluble guanidine salt to a boiling soln. of the alkali molybdatotungstate a series of guanidine derivatives was obtained.

J. J. Berzelius observed that a pale yellow precipitate of **uranyl tungstate,** UO_2WO_4, is formed when a soln. of a uranyl salt is treated with a soluble tungstate. J. Lefort obtained this salt from soln. of uranium acetate and sodium tungstate. The salt is insoluble in water, but soluble in strong acids, and in a soln. of ammonium carbonate. J. Lefort obtained **uranium tungstate,** $U(WO_4)_3.5H_2O$, as a yellow precipitate by treating uranyl acetate with sodium ditungstate ; if normal sodium tungstate is employed, the *dihydrate,* $UO_2(WO_4).2H_2O$, is formed as a yellow amorphous precipitate, sparingly soluble in water. O. W. Gibbs dissolved uranium trioxide in dil. sulphuric acid, treated the soln. with zinc, and then treated the insoluble, greyish-green powder with a soln. of sodium paratungstate, dark olive-green crystals of **sodium uranium tungstate,** $12Na_2O.6UO_2.8WO_3.25H_2O$, were formed. This is decomposed by nitric acid, and by boiling soda-lye. O. W. Gibbs prepared **potassium uranium tungstate,** $9K_2O.6UO_2.8WO_3.34H_2O$, in a similar way. It is insoluble in hot water and hydrochloric acid ; and it precipitates silver and mercury salts from soln. of their nitrates ; and it undergoes double decomposition with calcium and barium chlorides. **Ammonium uranium tungstate** was similarly prepared.

E. F. Anthon[16] treated a soln. of a manganous salt with normal sodium tungstate and obtained a greyish-white powder of **manganous tungstate,** $MnWO_4.2H_2O$. When the *dihydrate* is ignited it loses its water and becomes pale yellow, and finally melts. The dihydrate is not soluble in cold hydrochloric acid, but it is soluble in warm phosphoric or oxalic acid, and less soluble in boiling acetic acid. Potash-lye extracts the tungsten as trioxide from the dihydrate. A. Geuther and E. Forsberg melted a mixture of sodium tungstate, manganous chloride, and sodium chloride (1 : 2 : 2) in a covered crucible lined with magnesia ; extracted the cold mass with water ; and obtained pale brown crystals of the anhydrous salt $MnWO_4$. E. Zettnow said that if an excess of manganous chloride be employed, brownish-yellow needles are formed, and with an excess of sodium tungstate, a dirty canary-yellow crystalline powder ; and A. Geuther and E. Fosberg obtained dirty yellowish-green needles by using an excess of sodium chloride (5 : 1 : 16). The brown crystals form a canary-yellow powder of sp. gr. 6·7. E. K. Broch, and P. Groth and A. Arzruni found that the crystals are monoclinic with the axial ratio $a:b:c=0{\cdot}8315:1:0{\cdot}8651$, and $\beta=89°\ 38'$. E. K. Broch calculated from the X-radiograms, the lattice constants $a=4{\cdot}84$ A., $b=5{\cdot}76$ A., and $c=4{\cdot}97$ A. ; the axial ratios $a:b:c=0{\cdot}841:1:0{\cdot}863$, and $\beta=89°\ 7'$; with the calculated density 7·18. Twinning occurs about the (100)-plane. For natural crystals, *vide infra.* W. Jander found the electrical conductivity of the salt to be about 3000×10^{-6} at 970° ; and he calculated values for the diffusion coeff. W. Jander studied the action of magnesium oxide on manganese tungstate. A. Rogers and E. F. Smith prepared red crystals of **ammonium manganic tungstate,** $4(NH_4)_2O.Mn_2O_3.12WO_3.23H_2O$, by boiling an aq. soln. of ammonium paratungstate with manganic hydroxide and evaporating the clear liquid. A. Rosenheim and H. Schwer represented it $(NH_4)_4H_5[Mn(WO_4)_6].9H_2O$. According to A. Just, when a soln. of manganous sulphate is added to a boiling soln. of sodium tungstate, manganous tungstate is precipitated. Sodium persulphate is now added, and the soln. is boiled for 15 mins., the volume being kept constant. The dark red soln. is filtered from a small quantity of manganese dioxide, and, after a time, red crystals of **sodium permanganic tungstate,** $3Na_2O.5WO_3.MnO_2.18H_2O$, the colour of potassium dichromate, separate. The salt may be regarded as a double salt of sodium manganic tetratungstate and sodium tungstate, $Mn(NaWO_4)_4.Na_2WO_4$; or it may be represented according to A. Rosenheim and H. Schwer's formula $Na_6H_2[MnO(WO_4)_5].17H_2O$. Soln. of the salt decompose slowly in the cold, rapidly on heating, with deposition of manganese dioxide it can, however, be crystallized from soln. of sodium tungstate. Most metallic salt-soln. yield precipitates.

As indicated in connection with the history of tungsten, the mineral *wolfram* or **wolframite** was shown by J. J. and F. de Elhuyar[17] to be a tungstate of iron and manganese. E. Riotte, and H. Credner called the mineral **hübnerite** when the manganese largely predominates, $MnWO_4$, and A. Weisbach called it *manganowolframite.* A. Breithaupt described a manganese wolframite as *megabasite,* but C. F. Rammelsberg showed that it is a variety of hübnerite, and similar remarks apply to the blumite of K. L. T. Liebe. A nearly pure **ferrous tungstate,** $FeWO_4$, was described by K. L. T. Liebe under the name **ferberite**—after R. Ferber—A. Weisbach called it *ferrowolframite.* The mineral *reinite*—named after J. J. Rein—and described by K. von Fritsch, and O. Luedecke as a tetragonal ferrous tungstate, is now regarded as a pseudomorph after scheelite. F. L. Hess showed that there is a family group of minerals which can be grouped as wolframites with hübnerite, $MnWO_4$, and ferberite, $FeWO_4$, as end-members and with an indefinitely large number of intermediate manganous ferrous tungstates. For the purposes of classification, he suggested that hübnerite should be considered conventionally as manganous tungstate contaminated by not more than 20 per cent. of ferrous tungstate; ferberite, as ferrous tungstate contaminated by not more than 20 per cent. of manganous tungstate; and wolframite should come between these limits, being a mixture of ferrous and manganous tungstates containing not less than 20 per cent. and not more than 80 per cent. of either. E. T. Wherry proposed another arbitrary system based on the ratio Mn : Fe. If greater than 7 : 1, he called them *permanganowolframites;* if between 7 : 1 and 5 : 3, *domanganowolframites;* if between 5 : 3 and 3 : 5, *ferromanganowolframites;* if between 3 : 5 and 1 : 7, *ferrowolframites;* and if less than 1 : 7, *perferrowolframites.* Why not use the term 5 : 3-wolframite, and so on; or, using only one number if, say, Mn be conventionally made unity, the term 0·6-wolframite?

A. Geuther and E. Forsberg, and E. Zettnow obtained imitations of hübnerite, ferberite, and wolframite, with various proportions of iron and manganese by fusing sodium tungstate with different proportions of ferrous and manganous chlorides, and an excess of sodium chloride. Analyses of hübnerite were reported by W. Beck and N. Teich, I. Domeyko, J. B. Ekeley, H. F. Keller, F. A. Genth, F. N. Guild, W. P. Headden, F. L. Hess, W. F. Hillebrand, W. H. Hobbs, N. von Kulibin, A. H. Low, S. L. Penfield, C. F. Rammelsberg, etc. Analyses of ferberite were reported by W. Beck and N. Teich, F. A. Bernoulli, O. B. Bäggild, J. E. Carne, J. J. Ebelmen, J. B. Ekeley, L. L. Fermor, R. D. George, W. E. Greenawalt, F. L. Hess, K. L. T. Liebe, O. Luedecke, P. Nicolardot, C. F. Rammelsberg, R. Schneider, T. Wada, T. L. Walker, etc. Analyses of wolframite were reported by E. A. Atkinson, L. C. Ball, F. A. Bernoulli, J. J. Berzelius, A. W. G. Bleeck, G. Bodenbender, F. Bourion, C. A. Burghardt, A. Carnot, J. J. Ebelmen, A. M. Findlayson, P. Geiger, F. A. Genth, W. B. Giles, A. de Gramont, C. Granell, W. E. Greenawalt, F. N. Guild, F. L. Hess, F. Hoppe-Seyler, R. Helmhacker, W. Hempel, T. S. Hunt, J. D. Irving, A. Jahn, K. H. T. Kerndt, J. Lehmann, A. Liversidge, O. Luedecke, R. J. Meyer and H. Winter, P. Nicolardot, I. Pargo and A. Arango, P. Pondal and J. Vasquez-Garriga, A. Petzholdt, P. P. Pilipenko, G. J. Pöpplein, T. Richardson, B. Setlik, F. von Schaffgotsch, R. Schneider, O. J. Steinhart, L. Sipöcz, T. Thomson, L. N. Vauquelin, W. L. Walker, G. Weidinger, E. T. Wherry, etc.

The general formula for the whole family group is $(Fe,Mn)WO_4$. Magnesium and calcium oxides are commonly present to the extent of about a quarter per cent. A. Carnot reported 0·90 to 1·10 per cent. of tantalum pentoxide in a variety from Meymac; W. F. Hillebrand, 0·05 per cent. of columbium pentoxide in a sample from Ouray, California; L. Weiss, T. L. Phipson, A. Damour, and E. T. Wherry both tantalum and columbium pentoxides in samples from Cornwall, Arizona, etc.; G. Eberhard, H. S. Lukens, and H. Winter, scandium; G. Bodenbender, and F. A. Genth, stannic oxide, and copper oxide; E. A. Atkinson, and F. Hoppe-Seyler, indium oxide. Molybdenum may also be present. F. L. Hess, M. Kosaki, and W. T. Schaller reported Si, Al, Mg, Ca, Cr, Cb, Cu, Mo, Sc, Sr, Ti, and V to have been detected in ferberite by means of the spectroscope.

According to F. L. Hess, ferberite and wolframites are characteristically black;

hübnerite, reddish-brown, although some specimens are yellowish or nearly black. Except in the lighter coloured hübnerites, the presence of admixed ferberite cannot be detected by the eye. The dark-coloured varieties of the mineral are usually wolframites. Some specimens of hübnerite are almost garnet-red, but a specimen from Butte, Montana, is in part light yellowish-brown, and in part caramel-brown, while one from White Oaks, North Mexico, appears opaque black. Under the microscope, thin sections of hübnerite are light or dark yellowish-brown, or dark green by transmitted light. R. Tronquoy found that powdered hübnerite is sulphur yellow, and with plates of decreasing thickness the colour changes in different directions are: a, dark red to brown to pale brick-red to olive-green; b, bright red to orange-red to greenish-yellow; and c, orange-red to bright yellow with a faint green tinge. Usually the higher the proportion of ferric oxide, the blacker the colour; but the black mineral from White Oakes has only 0·55 per cent. of ferrous oxide, whereas lighter coloured hübnerite may contain more ferrous oxide. The cause of the dark colour is unknown. Hübnerite may be pleochroic with b yellowish-brown, and c, green. Ferberite is described by F. L. Hess as a black, opaque mineral which under the microscope may appear red by light transmitted through very thin edges—say 0·0001 to 0·0002 inch thick. Ferberite may occur coated with hydrated iron oxide, or be so intergrown with it that both the outside, and the parts exposed by fracture or cleavage may be brown. Some specimens are iridescent owing to thin films of oxide. The mineral may occur in bladed, irregularly lamellar, or columnar crystals; and also in granular, coherent masses. The crystals may be tabular or prismatic, and the faces in the prismatic zone may be vertically striated. The crystals of the wolframite family are all monoclinic, and V. Goldschmidt's value for the axial ratios $a:b:c$=0·8255 : 1 : 0·8664, and β=89° 32′ is typical of the whole series. Indeed, the crystallographic constants of the end-members do not show any characteristic differences. Ferberite has a greater tendency to form well-defined crystals than have the other members of the series. A. des Cloizeaux gave for the axial ratios of wolframite, $a:b:c$=0·8300 : 1 : 0·86781, and β=89° 21·6′; J. A. Krenner, 0·82447 : 1 : 0·86041, and β=89° 39′ 38″; and G. Seligmann, 0·82144 : 1 : 0·87111, and β=89° 34′; and for ferberite, P. Groth and A. Arzruni gave 0·8229 : 1 : 0·8462, and β=89° 22′.

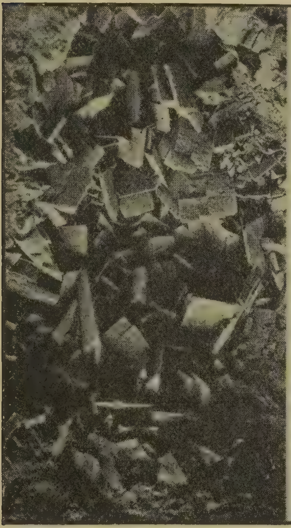


Fig. 47.—Wedge-shaped Crystals of Ferberite (×2).

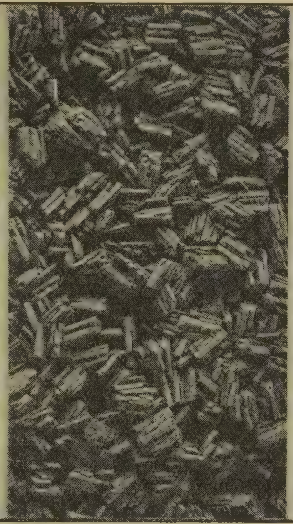


Fig. 48.—Rhomboidal Crystals of Ferberite (×1).

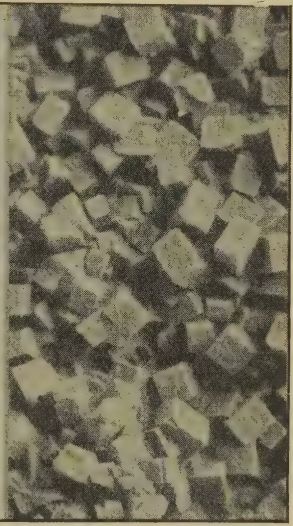


Fig. 49.—Cuboidal Crystals of Ferberite (×10).

R. Tronquoy gave $a : b : c = 0{\cdot}8315 : 1 : 0{\cdot}8651$, and $\beta = 90°\ 22'$ for hübnerite. F. Machatschky gave $0{\cdot}8362 : 1 : 0{\cdot}8668$, and $\beta = 89°\ 7\frac{1}{2}'$ for hübnerite, and $0{\cdot}8300 : 1 : 0{\cdot}8678$ and $\beta = 89°\ 22'$ for wolframite. E. K. Broch found that the crystals are like those of magnesium tungstate. The crystals of ferberite and wolframite are frequently wedge-shaped, Fig. 47 (Hoosier Mine, Colorado), and often in elongated rhomboids, Fig. 48 (Nugget Mine, Colorado), or in cubes, Fig. 49 (Georgia A. Mine, Colorado). These forms appear in ores where the crystals have grown in open cavities. The photographs, Figs. 47 to 49, are by F. L. Hess. Wolframite does not usually show good crystal boundaries, but occurs in tabular or irregular masses. Hübnerite has a marked tendency to form radiating groups of thin-bladed crystals, but dense, fine-grained aggregates of closely-packed crystals wherein irregular boundaries frequently occur. The shiny cleavage surfaces which are developed when these masses are broken may be mistaken for crystal faces. Wolframite rarely shows good external crystal forms; and it usually consists of irregular aggregates with no external crystal forms, and the individuals may have microscopic dimensions or be over 5 cms. in diameter. Crystals of all members of the series readily split along the (010)-plane. The plane cleavage is at right angles to the plane of elongation of the tabular forms. According to A. des Cloizeaux, parting is sometimes observed parallel to the (100)- and the (102)-planes. Twinning occurs about the c-axis, with (100) as the composition plane; G. Rose also gave (023) as a twinning plane. Observations on the crystals of wolframite were also made by C. Anderson, W. H. Miller, A. S. Eakle, P. Groth and A. Arzruni, P. von Jeremejeff, A. Jahn, K. Jimbo, F. Sandberger, L. J. Spencer, P. Geijer, F. L. Hess, and W. T. Schaller; the crystals of hübnerite were described by J. J. Bravo, E. Bertrand, S. L. Penfield, R. Tronquoy, F. L. Hess, D. J. Fisher, and W. T. Schaller; and those of ferberite by C. H. Warren, A. J. Moses, O. B. Böggild, F. L. Hess, and W. T. Schaller. P. Groth and A. Arzruni found the optic axial angles for red Li-light to be $2H_a = 93°$ and $2H_2 = 141°$; and $2V = 75°$. E. S. Larsen gave for hübnerite $2V = 73°$. The optical characters of wolframite and of hübnerite are positive. E. K. Broch calculated the following lattice-constants, in A-units, from the X-radiograms:

	a	b	c	β	$a : b : c$	Density
$MnWO_4$	4·84	5·76	4·97	89° 7′	0·841 : 1 : 0·863	7·18
Hübnerite	4·82	5·76	4·97	89° 7′	0·837 : 1 : 0·863	7·25
Wolframite	4·78	5·73	4·98	89° 34′	0·835 : 1 : 0·869	7·34
Ferberite	4·71	5·69	4·95	90° 0′	0·828 : 1 : 0·870	7·58
$FeWO_4$ (and reinite)	4·70	5·69	4·93	90° 0′	0·825 : 1 : 0·866	7·61

The sp. gr. of hübnerite is about 7·2 or 7·3. The artificial manganous tungstate prepared by A. Geuther and E. Forsberg had a sp. gr. of 7·1; A. Breithaupt gave for the mineral 7·14; R. Tronquoy, 7·09; P. Geijer, 7·283; and W. F. Hillebrand, 7·177 at 24°. The sp. gr. of ferberite is near 7·5, though A. Geuther and E. Forsberg gave for the artificial ferrous tungstate 7·1; and for the mineral, C. F. Rammelsberg gave 7·169, and A. Breithaupt, 6·801. L. Sipöcz gave 7·4581 for a variety with Fe : Mn = 2 : 1. O. Luedecke gave 6·640 for the sp. gr. of reinite. A. Geuther and E. Forsberg gave 7·0 for the sp. gr. of artificial $(0{\cdot}3Fe, 0{\cdot}7Mn)WO_4$; F. Mohs gave for wolframite 7·155, and A. F. Gehlen, 7·097. For the relation between sp. gr. of wolframite and the percentage amount of contained tungsten trioxide, the Wolf Tongue Milling Co. gave:

WO_3	1	5	10	15	20	25	30	35	40	44 per cent.
Sp. gr.	2·724	2·821	2·951	3·096	3·263	3·432	3·629	3·850	4·094	4·323

When the mineral is ground to an impalpable powder, or drawn over a surface of rough porcelain—the so-called streak of the mineral—the colour with ferberite is dark brown or nearly black, that of wolframite is dark brown to reddish-brown, and that of hübnerite is brownish-red or greenish-yellow. The hardness of ferberite is about 5, so that it is easily scratched by a pocket-knife, that of hübnerite is nearly the same—R. Tronquoy gave approximately 4 and added that the hardness on the (010)-face is smaller than that on the (001)-face—so also is the hardness of wolframite which is nearly 5. V. H. Regnault gave 0·09780 for the sp. ht. of crystals of wolframite between 6° and 98°; H. Kopp, 0·0930 between 21° and 53°; and G. Lindner, 0·09755 at 100°; 0·09840 at 200°; 0·09949 at 300°; and 0·10015 at 350°. E. S. Larsen gave $\beta=2{\cdot}40$ for the index of refraction of ferberite with Li-light, and added that the birefringence is large; for wolframite with Li-light, he found $\alpha=2{\cdot}26$–$2{\cdot}31$; $\beta=2{\cdot}32$; and $\gamma=2{\cdot}42$ to $2{\cdot}46$; and for hübnerite, with *D*-light, $\alpha=2{\cdot}17$–$2{\cdot}20$; $\beta=2{\cdot}22$; and $\gamma=2{\cdot}30$–$2{\cdot}32$. E. Wartmann, and F. Beijerinck found wolframite to be a non-conductor of electricity. C. Doelter gave for the electrical resistance, *R*, of wolframite:

	50°	150°	300°	400°	600°	780°	1000°	1100°
R . . .	11050	690	110	43·8	11·7	419	219	0·83

E. T. Wherry observed that ferberite is a good radio-detector. B. Bavink measured the magnetic properties of crystals of wolframite. A. Ambronn gave 241×10^{-6} mass units for the magnetic susceptibility, and G. Grenet, 35×10^{-6}. E. F. Smith found that wolframite dissolves when it is heated with sulphur monochloride. F. R. van Horn described replacements of wolframite by scheelite.

G. Tammann[18] observed that ferrous oxide reacts with tungsten trioxide between 480° and 700° forming **ferrous tungstate,** $FeWO_4$, and D. Balareff added that the reaction proceeds fastest at 700°. H. Debray obtained ferrous tungstate by strongly heating a mixture of tungsten trioxide and ferrous oxide in a current of hydrogen chloride; and A. Geuther and E. Forsberg prepared crystals of artificial ferberite by fusing together a mixture of sodium tungstate, ferrous chloride, and sodium chloride (1 : 2 : 2). E. Zettnow used a similar process. The lustrous, black crystals have a sp. gr. 7·1. For E. K. Broch's lattice-constants, *vide supra.* E. F. Anthon obtained the *trihydrate,* $FeWO_4.3H_2O$, as a light brown powder, by adding a soln. of a ferrous salt to one of sodium tungstate. The trihydrate is not dissolved by cold hydrochloric, sulphuric, or nitric acid, but it is completely dissolved by the boiling acids with the separation of tungsten trioxide; it is not soluble in water, but it is dissolved by boiling phosphoric acid, and by hot oxalic acid. J. Lefort found that the precipitate obtained by adding a soln. of normal or acid sodium tungstate to one of ferrous acetate produces a precipitate too unstable for analysis; but with a soln. of ferric acetate, definite ferric tungstates are formed, in the one case **ferric trioxytungstate,** $2Fe_2O_3.3WO_3.6H_2O$, or $Fe_2O_3.Fe_2(WO_4)_3.6H_2O$, and in the other case **ferric oxytungstate,** $Fe_2O_3.2WO_3.4H_2O$, or $Fe_2O(WO_4)_2.4H_2O$, or $Fe(OH)(WO_4).1\frac{1}{2}H_2O$. Both are yellow precipitates. 100 parts of water at 15° dissolve 33·3 parts of the former, and 2 parts of the latter. According to W. T. Schaller, the pale yellow, or brownish-yellow ochre from Deer Trail, Washington, consists of microscopic, hexagonal plates which are optically isotropic. The composition corresponds with ferric dioxytungstate, $Fe_2O_2(WO_4).6H_2O$, and he called the mineral **ferritungstite.** E. S. Larsen gave for the indices of refraction of ferritungstite, $\omega=1{\cdot}80$, and $\epsilon=1{\cdot}72$. S. Prakash and N. R. Dhar studied the properties of the hydrogel of ferric tungstate. A. Laurent reported a complex **potassium ferric tungstate,** $9K_2O.12H_2O.2Fe_2O_3.45WO_3+54H_2O$, to be formed by melting potassium carbonate and nitrate with an excess of wolframite, and digesting the mass with water. The salt separated from that soln. in large regular prisms. The soln. of the salt does not give the ordinary reactions for ferric iron. S. Prakash and N. R. Dhar prepared a hydrogel of ferric tungstate. A. Laurent obtained a basic salt $18K_2O.3H_2O.Fe_2O_3.45WO_3+54H_2O$; and **barium ferric tungstate,** $21BaO.2Fe_2O_3.45WO_3.27H_2O$. The formulæ are probably not correct, and A. Rosenheim and H. Schwer added that *ihre Darstellung ist nicht reproduzierbar*—*vide infra,* dodecatungstates.

F. de Carli[19] found that the heating curves of mixtures of cobaltous oxide and tungsten trioxide show that a reaction commences at about 255°. H. Schultze obtained crystals of **cobaltous tungstate,** $CoWO_4$, by melting a mixture of sodium tungstate, and cobaltous and sodium chlorides (1 : 2 : 2); E. Zettnow used the proportions 6 : 1 : 6. The monoclinic crystals are dark green, and non-magnetic. When powdered, the colour of the crystal is violet. E. F. Anthon obtained the anhydrous salt by calcining the hydrate. According to H. Schultze, and E. Zettnow, at a red-heat the product becomes greenish-blue, at a higher temp., bluish-black. E. K. Broch gave for the lattice constants, calculated from the X-radiograms, a=4·66 A., b=5·68 A., c=4·93 A., $a : b : c$=0·820 : 1 : 0·868, and β=90°; and the calculated density is 7·76. E. F. Anthon, and E. F. Smith and R. H. Bradbury treated a soln. of normal alkali tungstate with one of a cobaltous salt. The violet precipitate when washed and dried forms the *dihydrate*, $CoWO_4.2H_2O$, which loses its water at a red-heat; it is insoluble in water, and cold nitric acid; it is partially soluble in oxalic acid; and completely soluble in warm phosphoric or acetic acid. A. Carnot said that the grey precipitate produced by a cobaltous salt in soln. of ammonium tungstate becomes rose-red when dried. It easily oxidizes in air. Its composition is $8(NH_4)_2O.2CoO.15WO_3.3H_2O$. E. K. Broch found the crystals of the anhydrous salt to be monoclinic like those of the magnesium salt.

F. de Carli found that a mixture of nickelous oxide and tungsten trioxide shows evidence of combustion on the heating curve at 260°. H. Schultze obtained **nickel tungstate,** $NiWO_4$, by fusing a mixture of sodium tungstate, and nickel and sodium chlorides (1 : 2 : 2). The brown rhombic crystals have the appearance of zinc blende. E. K. Broch found that the crystals are monoclinic like those of the magnesium salt; and the lattice constants, calculated from the X-radiograms, are a=4·68 A., b=5·66 A., c=4·93 A., $a : b : c$=0·827 : 1 : 0·870, and β=89° 4′; and the calculated density is 7·78. F. W. Clarke and J. L. Davis gave 6·8846 for the sp. gr. at 20·5°, and 6·8522 for the sp. gr. at 22°. J. Lefort obtained the *trihydrate*, $NiWO_4.3H_2O$, and E. F. Anthon the *hexahydrate*, $NiWO_4.6H_2O$, as a pale green powder, by precipitation from mixtures of soln. of normal potassium tungstate and a nickel salt. It loses its water when heated to redness; it is insoluble in water, and soln. of oxalic acid; and it is soluble in boiling phosphoric and acetic acids, as well as in warm aq. ammonia. W. Jander gave about 600×10^{-6} for the electrical conductivity of nickel tungstate at 980°; and he also obtained values for the diffusion coeff. H. O. Schulze studied the action of tungstic acid on soln. of nickel chloride. G. L. Clark found the dissociation temp. of **nickel hexamminotungstate,** $NiWO_4.6NH_3$, to be 393° at 760 mm. According to A. Rogers and E. F. Smith, when hydrated nickel sesquioxide is boiled for 8 hrs. with an ammoniacal soln. of ammonium paratungstate, and the blue filtered soln. concentrated by evaporation, the soln. becomes green as the ammonia is expelled, and simultaneously deposits a green powder which redissolves if aq. ammonia is added forming a blue soln.; if the soln. be kept ammoniacal during the evaporation, a greenish-white, crystalline powder of **ammonium nickelic tungstate,** $3(NH_4)_2O.Ni_2O_3.16WO_4.22H_2O$, is formed. A second ammonium nickelic salt is formed, $(NH_4)_2O.Ni_2O_3.4WO_4.7H_2O$, if ammonia be passed through the soln. while it is being evaporated. The first salt is sparingly soluble in water once it has separated from soln., and, in consequence, salts are best obtained by double decomposition with the soln. before it is evaporated. In this way, barium chloride furnishes white, insoluble **barium nickelic tungstate,** $19BaO.Ni_2O_3.16WO_3$.

O. W. Gibbs[20] reported green or yellowish-green crystals of platinic decatungstate, $PtO_2.10WO_3.4H_2O$, to be formed by treating the barium salt with sulphuric acid, or the silver salt with hydrochloric acid; and pale yellow platinic cositungstate, $PtO_2.20WO_3.9H_2O$, by converting the corresponding sodium salt into the mercurous salt, adding hydrochloric acid, and spontaneously evaporating the filtrate. According to O. W. Gibbs, when platinic hydroxide is boiled with sodium paratungstate, two isomeric **sodium platinic decatungstates,** $4Na_2O.PtO_2.10WO_3.25H_2O$, are formed; one gives olive-green crystals, and the other honey-yellow prisms. They are readily soluble in water, and give flocculent or crystalline precipitates with the heavy metals, and the higher alkaloids. O. W. Gibbs reported that the deep orange soln. of platinic hydroxide in sodium paratungstate, furnishes, on standing, crystals of sodium platinic decatungstate, $6Na_2O.PtO_2.10WO_3.28H_2O$. According to A. Rosenheim, when a soln. of a paratungstate is boiled with platinic hydroxide, a large portion dissolves forming a deep red liquid; when the mixture is heated in a sealed tube at 250° to 300°, rather more platinic hydroxide dissolves, and a deep brownish-red liquid is formed, but in neither case could O. W. Gibbs' products be obtained. A. Rosenheim suggested that O. W. Gibbs' products consisted of paratungstates containing mechanically-occluded platinic hydroxide, coloured by partial reduction. Soln. of metatungstates dissolve platinic hydroxide in considerable quantities on boiling, and still more readily when heated in a sealed tube, although platinic hydroxide is quite insoluble in water, even when heated with it in a sealed tube at 300°; on evaporating these soln., even under diminished press., nothing but the unaltered reagents was obtained. When a conc. soln. of normal sodium tungstate is boiled with platinic hydroxide, the soln. becomes faintly yellowish, much less platinic hydroxide being dissolved than in the case of the acid salts; this is opposed to the view that platinic hydroxide acts as an acid. The strongly alkaline soln. is filtered as quickly as possible, and, on cooling, a neutral compound, exhibiting the reactions of a paratungstate, separates from the filtrate in small yellow needles of **sodium platinic heptatungstate,** $5Na_2O.7WO_3.2PtO_2.35H_2O$; this cannot be recrystallized, as it then undergoes decomposition; on this account a further yield is not obtained by concentrating the mother-liquor, and the compound cannot be prepared from dil. soln. of sodium metatungstate. It is a double salt of sodium paratungstate (1 mol.) and sodium platinate (2 mols.), as the following experiment proves. When the calculated quantities of sodium paratungstate and platinic hydroxide are boiled with sodium hydroxide soln., the same salt is formed, but this is not the case if sodium hydroxide is excluded. It appears, therefore, that platinic hydroxide has very weak acidic properties (comparable with those of alumina), which it exhibits only with such alkaline salts as normal tungstates; it dissolves in para- or meta-tungstates as a base.

O. W. Gibbs gradually added hydrochloroplatinic acid to a boiling soln. of sodium tungstate containing a considerable excess of sodium hydroxide, and treated the yellow soln. with an excess of acetic acid. Topaz-yellow crystals of **sodium platinic cositungstate,** $9Na_2O.PtO_2.20WO_3.58H_2O$, were formed. The salt loses water and oxygen when heated. It can be recrystallized without decomposition; the soln. is acidic to litmus. With ammonium chloride, the soln. gives a precipitate of sodium ammonium 1 : 4-paratungstate; thallous nitrate gives a granular precipitate—**thallous platinic cositungstate;** cobaltic hexamminotrichloride, pale brown plates—**cobaltic platinic hexamminocositungstate;** copper sulphate, a pale blue precipitate—**copper platinic cositungstate;** silver nitrate, a white precipitate—**silver platinic cositungstate;** and mercurous nitrate, a pale yellow, amorphous precipitate—**mercurous platinic cositungstate.** By boiling platinic hydroxide with sodium paratungstate honey-yellow crystals of **sodium platinic triacontatungstate,** $12Na_2O.PtO_2.30WO_3.72H_2O$, are formed. The salt is dehydrated on a water-bath. O. W. Gibbs also obtained sodium diplatinic triacontatungstate, $15Na_2O.2PtO_2.30WO_3.89H_2O$, in dull, yellow crystals, easily soluble in water, by the action of hydrochloroplatinic acid on sodium tungstate in the presence of an excess of sodium hydroxide, and then treating the soln. with an excess of acetic acid. The aq. soln. is acid to litmus, and with an ammonium salt furnishes **ammonium diplatinic triacontatungstate;** with a potassium salt, **potassium diplatinic triacontatungstate;** with barium chloride, **barium diplatinic triacontatungstate;** and with mercurous nitrate, **mercurous diplatinic triacontatungstate.**

O. W. Gibbs added that qualitative tests indicate that iridium, ruthenium, palladium, and osmium form similar salts.

REFERENCES.

[1] E. F. Anthon, *Repert. Pharm.*, **76**. 349, 1836; *Journ. prakt. Chem.*, (1), **8**. 399, 1836; (1), **9**. 337, 1836; J. C. G. de Marignac, *Ann. Chim. Phys.*, (3), **69**. 5, 1863; *Compt. Rend.*, **55**. 888, 1862; C. E. Guignet, *ib.*, **108**. 178, 1889; R. E. Liesegang, *Phot. Arch.*, **34**. 162, 1893; A. Rosenheim and F. Jacobsohn, *Zeit. anorg. Chem.*, **50**. 297, 1906; K. A. Hofmann and V. Kohlschütter, *ib.*, **16**. 463, 1898; E. Kunau, *Reindarstellung und Lumineszenz von Calcium-wolframat Cadmium -iodide, und Kalomel*, Greisswald, 1930; T. H. Tsao, *Chemie und Lumineszenz des Calcium wolframats*, Greisswald, 1928.

[2] G. C. Gmelin, *Schweigger's Journ.*, **30**. 173, 1820; *Gilbert's Ann.*, **62**. 399, 1819; **64**. 371, 1820; E. F. Anthon, *Repert. Pharm.*, **76**. 349, 1836; *Journ. prakt. Chem.*, (1), **8**. 399, 1836; (1), **9**. 337, 1836; A. Rosenheim and W. Reglin, *Zeit. anorg. Chem.*, **120**. 103, 1921; J. A. M. van Liempt, *ib.*, **143**. 285, 1925; F. Hoermann, *ib.*, **177**. 145, 1928; *Beitrag zur Kenntnis der Molybdate und Wolframate*, Leipzig, 1928; W. Zachariasen, *Tids. Norsk. Geol.*, **9**. 65, 1926.

[3] L. N. Vauquelin and L. Hecht, *Journ. Mines*, **4**. 19, 1796; F. Wöhler, *Pogg. Ann.*, **2**. 345, 1824; *Quart. Journ. Science*, **20**. 177, 1826; *Phil. Mag.*, **66**. 263, 1825; *Nachr. Gött.*, 35, 1850; *Liebig's Ann.*, **73**. 190, 1850; **77**. 262, 1851; *Ann. Chim. Phys.*, (2), **29**. 43, 1823; (3), **29**. 187, 1850; A. Riche, *Recherches sur le tungstène et ses composés*, Paris, 1857; (3), **50**. 15, 1857; V. Forcher, *Journ. prakt. Chem.*, (1), **86**. 227, 1862; *Bull. Soc. Chim.*, (2), **5**. 197, 1863; *Sitzber. Akad. Wien*, **44**. 165, 1861; E. F. Anthon, *Repert. Pharm.*, **76**. 349, 1836; *Journ. prakt. Chem.*, (1), **8**. 399, 1836; (1), **9**. 337, 1836; E. Zettnow, *Pogg. Ann.*, **130**. 46, 1867; C. F. Rammelsberg, *Handbuch der krystallographischen Chemie*, Leipzig, 193, 1855; B. von Pawlewsky, *Ber.*, **33**. 1223, 1900; S. Surawicz, *ib.*, **27**. 1306, 1904; R. Funk, *ib.*, **33**. 3700, 1900; F. Mauro and R. R. Panebianco, *ib.*, **15**. 2509, 1882; *Gazz. Chim. Ital.*, **12**. 180, 1882; *Atti Accad. Lincei*, (3), **6**. 205, 1882; F. W. Clarke and J. L. Davis, *Amer. Journ. Science*, (3), **14**. 281, 1877; W. G. Mixter, *ib.*, (4), **26**. 125, 1908; P. Burckhard, *Zeit. Chem.*, (2), **5**. 393, 1870; *Bull. Soc. Chim.*, (2), **14**. 35, 1870; B. Franz, *ib.*, (2), **16**. 238, 1871; *Journ. prakt. Chem.*, (2), **4**. 238, 1871; H. E. Boeke, *Zeit. anorg. Chem.*, **50**. 355, 1906; *Zeit. phys. Chem.*, **56**. 686, 1906; P. Walden, *ib.*, **1**. 529, 1887; J. W. Retgers, *ib.*, **8**. 6, 1891; W. Herz, *ib.*, **98**. 98, 1921; O. H. Wagner, *ib.*, **131**. 409, 1928; *Ueber die Brechungsexponenten einiger geschmolzener Salze*, Leipzig, 1927; A. Lottermoser, *Zeit. Koll.*, **121**. 243, 1922; M. Kröger, *ib.*, **30**. 16, 1922; J. C. G. de Marignac, *Ann. Chim. Phys.*, (3), **69**. 5, 1863; *Compt. Rend.*, **55**. 888, 1862; W. Zachariasen, *Tids. Norsk. Geol.*, **9**. 65, 1926; N. Parravano, *Gazz. Chim. Ital.*, **39**. ii, 55, 1909; J. J. Coleman, *Phil. Mag.*, (5), **23**. 1, 1887; F. J. Faktor, *Pharm. Post*, **34**. 485, 1901; A. Krefting, *Chem. Ind.*, **21**. 508, 1899; C. Scheibler, *Tagebl. deut. Naturf. Aerzte*, **45**. 114, 1872; *Zeit. Naturwiss. Halle*, **40**. 298, 1872; *Ber.*, **5**. 801, 1872; *Bull. Soc. Chim.*, (2), **19**. 23, 1873; O. Maschke, *Zeit. anal. Chem.*, **16**. 427, 1877; R. E. Liesegang, *Phot. Arch.*, **34**. 177, 1893; J. H. Long, *Journ. Amer. Soc.*, **17**. 87, 1894; W. K. van Haagen and E. F. Smith, *Journ. Amer. Chem. Soc.*, **33**. 1505, 1911; E. F. Smith, *Ber.*, **13**. 753, 1880; *Chem. News*, **43**. 61, 1881; **129**. 198, 207, 240, 257, 286, 1924; *Journ. Amer. Chem. Soc.*, **44**. 2027, 1922; R. G. Wells, *ib.*, **29**. 112, 1907; C. Watkins and H. C. Jones, *ib.*, **37**. 2626, 1916; H. Corimmboeuf, *Compt. Rend.*, **115**. 823, 1892; P. Hautefeuille, *ib.*, **84**. 1301, 1877; **85**. 952, 1877; P. Hautefeuille and A. Perrey, *ib.*, **110**. 334, 1890; J. Lefort, *ib.*, **92**. 1461, 1881; *Journ. Pharm. Chim.*, (5), **4**. 221, 1881; D. Gernez, *Compt. Rend.*, **104**. 783, 1887; E. Schaefer, *Beiträge zur Kenntnis der Wolframverbindungen*, Berlin, 1903; *Zeit. anorg. Chem.*, **38**. 143, 1904; H. S. van Klooster, *ib.*, **69**. 135, 1910; K. Hüttner and G. Tammann, *ib.*, **43**. 215, 1905; G. Tammann, *Mem. Acad. Petersbourg*, (7), **35**. 1, 1887; H. S. van Klooster and H. C. Germs, *ib.*, **86**. 369, 1914; J. Eltzbacher, *Beiträge zur Elektrochemie der Wolframate*, Berlin, 10, 1899; B. Kellner, *Untersuchungen über Perwolframate*, Berlin, 1909; H. Traube, *Neues Jahrb. Min.*, i, 195, 1894; I. Traube, *Zeit. anorg. Chem.*, **8**. 12, 1895; *Ber.*, **24**. 3074, 1891; F. Ullik, *Sitzber. Akad. Wien*, **56**. 148, 1867; *Journ. prakt. Chem.*, (1), **103**. 147, 1868; *Bull. Soc. Chim.*, (2), **11**. 50, 1869; J. W. Swan and J. A. Kendall, *Brit. Pat. No.* 3509, 1895; J. A. M. van Liempt, *Zeit. anorg. Chem.*, **122**. 175, 1922; **143**. 285, 1925; **181**. 425, 1929; H. Grossmann and H. Krämer, *ib.*, **41**. 43, 1904; L. Pissarjewsky, *ib.*, **24**. 108, 1900; F. M. Jäger, *ib.*, **101**. 183, 1917; F. M. Jäger and H. C. Germs, *Zeit. anorg. Chem.*, **119**. 161, 1921; F. M. Jäger and B. Kapma, *ib.*, **113**. 27, 1920; A. Rosenheim, *ib.*, **7**. 176, 1894; F. M. Jäger and J. Kahn, *Proc. Acad. Amsterdam*, **19**. 381, 1916; H. C. Germs, *De thermische Analyse van Loodsulfaat, -chromaat, -molybdaat, en -wolfraamaat en van hun binaire Combinaties*, Groningen, 1917; E. Herlinger, *Zeit. Kryst.*, **62**. 454, 1925; M. Amadori, *Atti Accad. Lincei*, (5), **22**. i, 453, 609, 1913; W. I. Baragiola, *Ueber das Verhalten der normalen Natrium-Kaliumsalze des Wolframs, Molybdäns, und Vanadins gegen Ammoniumchlorid*, Berlin, 1902; R. Lorenz and W. Herz, *Zeit. anorg. Chem.*, **120**. 320, 1922; **135**. 374, 1924; **138**. 330, 1924; H. Schulz and G. Jander, *ib.*, **162**. 141, 1927; V. I. Spitzin and L. Kaschtanoff, *ib.*, **157**. 141, 1926; V. Spitzin, *Zeit. anal. Chem.*, **75**. 440, 1928; *Zeit. anorg. Chem.*, **148**. 69, 1925; W. Biltz and W. Klemm, *ib.*, **152**. 267, 1926; F. Hoermann, *ib.*, **177**. 145, 1928; *Beitrag zur Kenntnis der Molybdate und Wolframate*, Leipzig, 1928; F. Bourion, *Ann. Chim. Phys.*, (8), **21**. 97, 1910; A. Laurent, *ib.*, (3), **21**. 62, 1847; H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, **1**. 319, 1851; E. Wegelin, *Zur Kenntnis einiger Natriumwolframate*, Zürich, 1906; F. Zambonini, *Sulle soluzioni solide dei composti di calcio, stronzio, bario e piombo con quelli delle " terre rare " e loro importanza per la mineralogia Chimica*, Padova, 1915; *Atti Accad. Lincei*, (5), **22**. i, 519, 1913; *Zeit. Kryst.*, **58**. 226, 1923; *Riv. Ital. Min.*, **45**. 1, 1915; L. Kahlenberg and W. J. Trautmann, *Trans. Amer. Electrochem. Soc.*, **39**. 377, 1921; E. Blanc,

Journ. Chim. Phys., **18**. 28, 1920 ; A. Hare, *Phil. Mag.*, (6), **48**. 412, 1924 ; C. N. Fenner, *Amer. Journ. Science*, (4), **36**. 331, 1913 ; *Zeit. anorg. Chem.*, **85**. 133, 1913 ; C. J. van Nieuwenburg and C. N. G. de Nooijer, *Rec. Trav. Chim. Pays-Bas*, **47**. 627, 1928 ; A. V. Dumansky and S. I. Diatschkovsky, *Journ. Russ. Phys. Chem. Soc.*, **60**. 1053, 1928 ; *Koll. Keit.*, **48**. 49, 1929 ; W. V. Bhagwat and N. R. Dhar, *Journ. Indian Chem. Soc.*, **6**. 781, 1929 ; G. Gore, *Electrochemistry*, London, 99, 1906 ; E. Bruchhaus, *Ueber Reaktionen zwischen gelösten Stoffen und Gasen bei Belichtung mit ultravioletten Strahlen*, Düsseldorf, 1930 ; F. Krauss and E. Bruchhaus, *Zeit. anorg. Chem.*, **189**. 53, 1930 ; P. Kordes, *Zeit. phys. Chem.*, **152**. 161, 1931 ; W. Jander and A. Winkel, *ib.*, **149**. 97, 1930 ; W. Lotz, *Leibig's Ann.*, **91**. 70, 1854 ; P. Krishnamurti, *Indian Journ. Phys.*, **5**. 633, 651, 1930.

[4] E. Zettnow, *Pogg. Ann.*, **130**. 46, 1867 ; E. F. Anthon, *Repert. Pharm.*, **76**. 349, 1836 ; *Journ. prakt. Chem.*, (1), **8**. 399, 1836 ; (1), **9**. 337, 1836 ; H. Schultze, *ib.*, (1), **90**. 201, 1863 ; *Ueber die Darstellung krystallisirter Verbindungen insbesondere über einige krystallisirte molybdänsaure und wolframsaure Salze*, Göttingen, 1862 ; *Liebig's Ann.*, **126**. 56, 1863 ; F. Wöhler and F. Rautenberg, *ib.*, **114**. 120, 1860 ; H. Schiff, *ib.*, **123**. 39, 1862 ; R. E. Liesegang, *Phot. Arch.*, **34**. 180, 1893 ; F. Fouqué and A. Michel-Lévy, *Synthèse des mineraux et des roches*, Paris, 191, 1882 ; I. Domeyko, *Ann. Mines*, (6), **16**. 537, 1869 ; P. Ray and J. Dasgupta, *Journ. Indian Chem. Soc.*, **5**. 519, 1928 ; S. H. C. Briggs, *Journ. Chem. Soc.*, **85**. 672, 1904 ; J. D. Whitney, *Proc. California Acad.*, **3**. 287, 1866 ; M. Adam, *Tableau minéralogique*, Paris, 32, 1869 ; G. W. Card, *Rec. Geol. Sur. N.S.W.*, **5**. 121, 1897 ; W. Muthmann, *Ber.*, **20**. 983, 1887 ; E. F. Smith and R. H. Bradbury, *ib.*, **24**. 2930, 1891 ; H. Traube, *Neues Jahrb. Min. B.B.*, **7**. 232, 1890 ; O. Widman, *Bull. Chim. Soc.*, (2), **20**. 64. 1873 ; G. Tammann, *Zeit. anorg. Chem.*, **149**. 35, 1925 ; L. Michel, *Bull. Soc. Min.*, **2**. 142, 1879 ; *Recherches sur quelques tungstates, molybdates, séléniates, tellurates cristallisés*, Paris, 1889.

[5] G. Carobbi, *Atti Accad. Lincei*, (5), **32**. ii, 79, 1923 ; *Gazz. Chim. Ital.*, **54**. 59, 1924 ; A. M. Findlayson, *Trans. N.Z. Inst.*, **40**. 110, 1907 ; E. F. Anthon, *Repert. Pharm.*, **76**. 349, 1836 ; *Journ. prakt. Chem.*, (1), **8**. 399, 1836 ; (1), **9**. 337, 1836 ; E. Zettnow, *Pogg. Ann.*, **130**. 46, 1867 ; C. G. Hoffmann, *Rept. Canada Geol. Sur.*, **6**. 21, 1890 ; C. Anderson, *Rec. Australian Museum*, **6**. 414, 1907 ; K. Becker and H. Becker-Rose, *Zeit. Physik*, **29**. 343, 1924 ; J. G. Wallerius, *Mineralogia*, Stockholm, 268, 303, 1747 ; A. Cronstedt, *Akad. Handl. Stockholm*, **21**. 227, 1751 ; C. W. Scheele, *ib.*, **2**. 89, 1781 ; *Journ. Phys.*, **22**. 724, 1783 ; A. Breithaupt, *Kurze Charakteristik des Mineralsystems*, Freiberg, 23, 1820 ; *Vollständige Charakteristik des Mineralsystems*, Dresden, 227, 1832 ; A. G. Werner, *Berg. Journ.*, 386, 1789 ; R. J. Haüy, *Traité de minéralogie*, Paris, **4**. 311, 1801 ; C. C. Leonhard, *Handbuch der Oryktognosie*, Heidelberg, 594, 189 ; C. J. B. Karsten, *Schweigger's Journ.*, **65**. 394, 1832 ; D. L. G. Karsten, *Mineralogische Tabellen*, Berlin, 56, 1800 ; C. von Linnaeus, *Systema naturæ*, Lugduni Batavorum, 1768 ; K. Endell, *Sprech.*, **44**. 185, 1911 ; F. M. Jäger and H. Haga, *Proc. Acad. Amsterdam*, **18**. 1350, 1916 ; H. Kopp, *Liebig's Ann. Suppl.*, **3**. 289, 1865 ; A. Russell, *Min. Mag.*, **19**. 19, 1920 ; *Atti Accad. Lincei*, (6), **7**. 660, 1928 ; G. Flink, *Bull. Geol. Inst. Upsala*, **5**. 96, 1900 ; L. Weiss, *Zeit. anorg. Chem.*, **65**. 314, 1910 ; D. Balareff, *ib.*, **160**. 92, 1927 ; G. Tammann, **149**. 21, 1925 ; **160**. 101, 1927 ; F. A. Henglein, *ib.*, **120**. 77, 1922 ; W. Jander, *ib.*, **166**. 31, 1927 ; **174**. 11, 1928 ; **191**. 171, 1930 ; **192**. 286, 295, 397, 1930 ; F. Ullik, *Sitzber. Akad. Wien*, **56**. 152, 1867 ; *Journ. prakt. Chem.*, (1), **103**. 147, 1868 ; *Bull. Soc. Chim.*, (2), **11**. 50, 1869 ; L. A. Hallopeau, *ib.*, (3), **31**. 1034, 1904 ; *Compt. Rend.*, **139**. 283, 1904 ; W. Löwinthal, *Ueber die Röntgenlumineszenz der Calciumwolframate und einiger anderer röntgenlumineszierender Körper*, Freiburg, 1908 ; D. Vorländer and H. Hempel, *Ber.*, **60**. B, 845, 1927 ; A. Schleede and T. H. Tsao, *ib.*, **62**. B, 763, 1929 ; T. H. Tsao, *Chemie und Lumineszenz des Calcium wolframats*, Greisswald, 1928 ; A. des Cloizeaux, *Nouvelles recherches sur les propriétés optiques des cristaux*, Paris, 1867 ; M. H. Klaproth, *Beiträge zur chemischen Kenntniss der Mineralkörper*, Berlin, **3**. 44, 1802 ; J. J. Berzelius, *Afhand. Fis. Kemi. Min.*, **4**. 305, 1815 ; *Ann. Chim. Phys.*, (2), **17**. 13, 1825 ; *Pogg. Ann.*, **4**. 147, 1825 ; **8**. 267, 1826 ; *Schweigger's Journ.*, **16**. 476, 1816 ; *Ann. Phil.*, **3**. 245, 1814 ; R. Brandes and C. F. Bucholz, *Schweigger's Journ.*, **20**. 285, 1817 ; B. K. Almström, *Geol. Für. Förh. Stockholm*, **47**. 135, 1925 ; A. Roemer, *Zeit. deut. geol. Ges.*, **15**. 607, 1863 ; E. Tiede and A. Schleede, *Zeit. Elektrochem.*, **29**. 305, 1923 ; F. A. Bernoulli, *Pogg. Ann.*, **111**. 607, 1860 ; E. Cane, *Rend. Accad. Napoli*, (3), **32**. 83, 1926 ; M. Choubine, *Russ. Ann. Mines*, 317, 1841 ; A. Delesse, *Bull. Geol. Soc.*, (2), **10**. 17, 1853 ; L. Kahlenberg and W. J. Trautmann, *Trans. Amer. Electrochem. Soc.*, **39**. 377, 1921 ; F. E. Swindells, *Journ. Amer. Opt. Soc.*, **16**. 165, 1928 ; D. Lovisato, *Atti Accad. Lincei*, (5), **16**. i, 632, 1907 ; A. Pochettino, *ib.*, (5), **13**. i, 301, 1904 ; F. de Carli, *ib.*, (6), **1**. 533, 1925 ; L. Colomba, *ib.*, (5), **15**. i, 281, 1905 ; A. Serra, *ib.*, (5), **18**. ii, 630, 1909 ; F. Rodolico, *ib.*, (6), **7**. 660, 1928 ; W. Arnold, *Wied. Ann.*, **61**. 321, 1897 ; J. J. Saslawsky, *Zeit. Kryst.*, **59**. 170, 1923 ; W. Ducca, *Ueber lumineszierende Stoffe und die Radioaktivität des Urans*, München, 1905 ; G. Ogden, *La Nature*, **24**. ii, 175, 1896 ; K. Keilhack, *Natur. Rund.*, **14**. 415, 1899 ; *Zeit. deut. geol. Ges.*, **50**. 131, 1899 ; F. Dreuschuch, *Fortschr. Röntgenstrahlen*, **4**. 180, 1901 ; R. J. Strutt, *Phil. Mag.*, (6), **6**. 250, 1903 ; G. F. Kunz and C. Baskerville, *Chem. News*, **89**. 1, 1904 ; P. Schuhknecht, *Untersuchungen über ultraviolette Fluoreszenz durch Röntgender Kathodenstrahlen*, Leipzig, 1905 ; A. D. Cox, *Bull. U.S. Geol. Sur.*, 652, 1917 ; M. D. Draper, *ib.*, 652, 1917 ; G. T. Lindroth, *Geol. För. Förh. Stockholm*, **44**. 110, 1922 ; **46**. 168, 1924 ; P. Berberich, *Jahrb. Berg. Hütt.*, 48, 1914 ; B. Setlik, *Chem. Ztg.*, **13**. 1474, 1889 ; E. Hugi, *Mitt. Naturforsch. Ges. Bern*, 12, 1919 ; H. Hirschi, *Schweiz. Min. Pet. Mitt.*, **3**. 160, 1923 ; L. Vegard, *Phil. Mag.*, (7), **1**. 1151, 1926 ; L. Vegard and A. Refsum, *Norske Vid. Akad*

Skr., 2, 1927 ; F. C. Henrici and J. F. L. Hausmann, *Gött. Ver. Berg. Freunde*, **4**. 215, 1843 ; E. Wartmann, *Mem. Sciences Geneve*, (1), **12**. 1, 1853 ; T. Barth, *Norsk. Geol. Tids.*, **9**. 23, 1926 ; F. Beijerinck, *Neues Jahrb. Min. B.B.*, **11**. 403, 1897 ; T. A. L. du Moncel, *Lumière élect.*, **7**. 73, 1882 ; *Compt. Rend.*, **81**. 514, 1875 ; **92**. 39, 1881 ; J. J. Rubber, *Mining Scient. Press.*, **133**. 11, 1916 ; F. Machatschky, *Zeit. Kryst.*, **67**. 163, 1928 ; E. E. Fairbanks, *Econ. Geol.*, **21**. 399, 1926 ; J. A. Hedvall and N. von Zweigbergk, *Zeit. anorg. Chem.*, **108**. 119, 1919 ; J. Lefort, *Compt. Rend.*, **88**. 798, 1876 ; *Recherches chimiques sur les tungstates*, Paris, 1878 ; *Ann. Chim. Phys.*, (5), **9**. 99, 1876 ; (5), **15**. 326, 1878 ; (5), **17**. 476, 1879 ; (6), **22**. 195, 1891 ; N. S. Manross, *Liebig's Ann.*, **81**. 243, 1852 ; H. Schultze, *Ueber die Darstellung krystallisirter Verbindungen insbesondere über einige krystallisirte molybdänsäure und wolframsäure Salze*, Göttingen, 1862 ; *Liebig's Ann.*, **126**. 56, 1863 ; A. Drevermann, *ib.*, **89**. 11, 1854 ; A. Geuther and E. Forsberg, *ib.*, **120**. 270, 1861 ; *Gött. Nachr.*, 225, 1861 ; J. Eyerman, *Minerals of Pennsylvania*, Easton, Pa., 1911 ; H. Debray, *Compt. Rend.*, **55**. 287, 1862 ; E. Jannetaz, *ib.*, **114**. 1352, 1892 ; A. Radiguet, *ib.*, **124**. 179, 1897 ; C. de Rohden, *ib.*, **159**. 318, 1914 ; A. Carnot, *ib.*, **79**. 638, 1874 ; A. Macé, *ib.*, **36**. 825, 1853 ; S. H. C. Briggs, *Journ. Chem. Soc.*, **85**. 672, 1904 ; J. O. Perrine, *Phys. Rev.*, (2), **22**. 48, 1923 ; S. Traverso, *Resoccontio Riunioni Soc. Min. Sarda*, (8), **6**. 8, 1901 ; F. A. Genth, *Amer. Journ. Science*, (2), **28**. 252, 1859 ; G. T. Bowen, *ib.*, (1), **5**. 118, 1822 ; F. W. Clarke and J. L. Davis, *ib.*, (3), **14**. 281, 1877 ; M. Bauer, *Crystallographische Untersuchung des Scheelits*, Würtemberg, 1871 ; *Würtemberg. Ver. Nat. Jahresb.*, **27**. 129, 1871 ; *Pogg. Ann.*, **143**. 452, 1871 ; *Neues Jahrb. Min.*, 879, 1871 ; S. Koch, *Földt. Közl.*, **54**. 85, 1925 ; *Ann. Musei Hungarici*, **22**. 142, 1925 ; E. F. Smith, *Journ. Amer. Chem. Soc.*, **20**. 289, 1898 ; E. F. Smith and R. H. Bradbury, *Centr. Min.*, 727, 1903 ; H. Traube, *ib.*, 679, 1901 ; *Neues Jahrb. Min. B.B.*, **7**. 232, 1890 ; L. Michel, *Recherches sur quelques tungstates, molybdates, séléniates, tellurates cristallisés*, Paris, 1889 ; *Bull. Soc. Min.*, **2**. 142, 1879 ; A. de Schulten, *ib.*, **26**. 112, 1903 ; A. Lacroix, *ib.*, **31**. 349, 1908 ; C. H. Boissevain and W. F. Drea, *Phys. Rev.*, (2), **31**. 851, 1928 ; A. Cossa, *Atti Accad. Lincei*, (3), **3**. 25, 1879 ; (3), **4**. 233, 1880 ; *Compt. Rend.*, **87**. 377, 1878 ; *Gazz. Chim. Ital.*, **9**. 118, 1879 ; **10**. 467, 1880 ; *Ricerche chimiche e microscopiche su rocciie e minerali d'Italia, Torino*, 287, 1881 ; F. Zambonini, *Atti Accad. Lincei*, (5), **15**. i, 558, 1906 ; *Zeit. Kryst.*, **41**. 61, 1905 ; *Sulle soluzioni solide dei composti di calcio, stronzio, bario, e piombo con quelli della " terre rare " e loro importanza per la mineralogia chimica*, Padova, 1915 ; *Riv. Ital. Min.*, **45**. 1, 1915 ; *Zeit. Kryst.*, **12**. 411, 1887 ; C. Schmidt, *ib.*, **24**. 137, 1895 ; **36**. 160, 1902 ; H. Saegusa, *Scient. Rep. Tohoku Univ.*, **11**. 463, 1922 ; J. W. Retgers, *Zeit. phys. Chem.*, **8**. 6, 1891 ; M. L. Huggins, *Phys. Rev.*, (2), **21**. 719, 1923 ; C. Scheibler, (1), **80**. 204, 1860 ; *Journ. prakt. Chem.*, (1), **83**. 273, 1861 ; *Chem. News*, **6**. 181, 1862 ; *Sitzber. Akad. Berlin*, 208, 1860 ; *De wolframiatibus*, Königsberg, 1861 ; M. G. Bogoslovsky, A. A. Mamurovsky and P. V. Savitzkaya, *Russ. Pat. No.* 5013, 1928 ; H. Dauber, *Pogg. Ann.*, **107**. 272, 1859 ; V. M. Goldschmidt, *Geochem. Vert. Ges.*, **7**. 2, 1926 ; C. F. Rammelsberg, *Pogg. Ann.*, **78**. 514, 1849 ; *Zeit. deut. geol. Ges.*, **19**. 493, 1867 ; P. Groth, *Die Mineraliensammlung der Kaiser Wilhelms Universität Strassburg*, Strassburg, 157, 1868 ; G. vom Rath, *Ber. Niederrh. Ges. Bonn*, 215, 1882 ; J. Block, *ib.*, 68, 1906 ; E. K. Broch, *Zeit. phys. Chem.*, **1**. B, 409, 1928 ; *Norske Vid. Akad. Skr.*, 8, 1929 ; R. G. Dickinson, *Journ. Amer. Chem. Soc.*, **45**. 85, 1920 ; V. R. von Zepharovich, *Lotos.*, **34**. 81, 1885 ; *Mineralogisches Lexicon für das Kaiserthum Oesterreich*, Wien, 1885 ; L. J. Igelström, *Geol. För. Förh. Stockholm*, **13**. 122, 1891; E. Péchard, *Ann. Chim. Phys.*, (6), **22**. 202, 1891 ; J. R. Partington, *Nature*, **125**. 636, 1930; T. Hiortdahl, *Zeit. Kryst.*, **12**. 411, 1887 ; W. Jander and W. Stamm, *Zeit. anorg. Chem.*, **190**. 95, 1930 ; W. Jander, *ib.*, **190**. 397, 1930 ; **191**. 171, 1930 ; **192**. 286, 295, 1930 ; E. Kunau, *Reindarstellung und Lumineszenz von Calcium-wolframat, Cadmium-jodid und Kalomel*, Greisswald, 1930 ; I. I. Navano and J. Palacios, *Anal. Fis. Quim.*, **72**. 846, 1929 ; F. R. van Horn, *Amer. Min.*, **15**. 460, 1930 ; W. Florence, *Centr. Min.*, 725, 1903.

[6] G. Tammann, *Zeit. anorg. Chem.*, **149**. 21, 1925 ; E. F. Anthon, *Repert. Pharm.*, **76**. 349, 1836 ; *Journ. prakt. Chem.*, (1), **8**. 399, 1836 ; (1), **9**. 337, 1836 ; J. Lefort, *Compt. Rend.*, **88**. 798, 1876 ; *Recherches chimiques sur les tungstates*, Paris, 1878 ; *Ann. Chim. Phys.*, (5), **9**. 99, 1876 ; (5), **15**. 326, 1878 ; (5), **17**. 476, 1879 ; F. A. Bernoulli, *Pogg. Ann.*, **111**. 607, 1860; W. Lotz, *Liebig's Ann.*, **91**. 49, 1854 ; C. W. Balke and E. F. Smith, *Journ. Amer. Chem. Soc.*, **25**. 1229, 1903 ; L. C. Daniels, *ib.*, **30**. 1846, 1908 ; *Derivatives of Complex Inorganic Acids*, Philadelphia, 1908 ; A. Rogers and E. F. Smith, *Journ. Amer. Chem. Soc.*, **26**. 1474, 1904.

[7] C. Renz, *Beiträge zur Kenntnis des Indiums und Thalliums*, Breslau, 1902 ; *Ber.*, **34**. 2763, 1901 ; H. Flemming, *Jena. Zeit.*, **4**. 34, 1868 ; *Bull. Soc. Chim.*, (2), **10**. 235, 1868 ; E. Schaefer, *Beiträge zur Kenntnis der Wolframverbindungen*, Berlin, 1903 ; *Zeit. anorg. Chem.*, **38**. 171, 1904 ; P. S. Oettinger, *On the Combinations of Thallium*, Berlin, 30, 1864 ; *Zeit. Chem.*, (1), **7**. 440, 1864.

[8] G. Tammann, *Zeit. anorg. Chem.*, **149**. 21, 1925 ; G. Tammann and W. Rosenthal, *ib.*, **156**. 20, 1926 ; A. Cossa, *Gazz. Chim. Ital.*, **9**. 118, 1879 ; **10**. 467, 1880 ; **16**. 284, 1886 ; A. Cossa and M. Zecchini, *ib.*, **10**. 225, 1880 ; G. Carobbi and G. Tancredi, *ib.*, **58**. 45, 1928 ; F. Zambonini, *Sulle soluzioni solide dei composti di calcio, stronzio, bario, e piombo con quelli delle " terre rare " e loro importanza per la mineralogia chimica*, Padova, 1915 ; *Atti Accad. Lincei*, (5), **15**. i, 558, 1906 ; (5), **22**. i, 519, 1913 ; *Zeit. Kryst.*, **41**. 61, 1905 ; **58**. 226, 1923 ; *Riv. Ital. Min.*, **45**. 1, 1915 ; P. Didier, *Compt. Rend.*, **102**. 823, 1886 ; A. J. Högbom, *Bull. Soc. Chim.*, (2), **42**. 2, 1884 ; *Oefvers. Svenska Akad. Förh.*, **40**. 5, 1884 ; A. Rogers and E. F. Smith, *Journ. Amer. Chem. Soc.*, **26**. 1474, 1904 ; F. R. M. Hitchcock, *ib.*, **17**. 483, 1895 ; H. Traube, *Centr. Min.*, 679, 1901 ; P. T. Cleve, *Oefvers. Svenska Akad. Förh.*, **40**. 7, 1883 ; *Bull. Soc. Chim.*, (2), **43**.

162, 1885; *Chem. News*, **53**. 93, 1886; A. Cleve, *ib.*, **86**. 248, 1902; *Oefvers. Svenska Akad. Förh.*, **58**. 573, 1902; *Zeit. anorg. Chem.*, **32**. 152, 1902.

[9] O. Kulka, *Beiträge zur Kenntnis einiger Zirkoniumverbindungen*, Bern, 1902; L. A. Hallopeau, *Bull. Soc. Chim.*, (3), **15**. 917, 1896; *Compt. Rend.*, **122**. 1419, 1896; G. N. Wyrouboff, *Bull. Soc. Min.*, **19**. 285, 1896; W. Nernst, *German Pat., D.R.P.* 184704, 1896; J. J. Berzelius, *Pogg. Ann.*, **16**. 385, 1829; A. J. Högbom, *Bull. Soc. Chim.*, (2), **42**. 2, 1884; *Oefvers. Svenska Akad. Förh.*, **40**. 5, 1884.

[10] F. de Carli, *Atti Accad. Lincei*, (6), **1**. 533, 1925; E. F. Anthon, *Journ. prakt. Chem.*, (1), **9**. 341, 1836; G. von Knorre, *ib.*, (2), **27**. 94, 1883; W. Lotz, *Liebig's Ann.*, **91**. 49, 1854; S. Prakash and N. R. Dhar, *Journ. Indian Chem. Soc.*, **6**. 391, 587, 1929.

[11] A. Breithaupt, *Kurze Charakteristik des Mineralsystems*, Freiberg, 14, 1820; F. S. Beudant, *Traité élémentaire de minéralogie*, Paris, **2**. 662, 1832; W. Haidinger, *Handbuch der bestimmenden Mineralogie*, Wien, 504, 1845; A. Lévy, *Description d'une collection de minéraux formée par M. Henri Heuland*, Londres, **2**. 473, 1837; *Pogg. Ann.*, **8**. 513, 1826; *Ann. Phil.*, **28**. 364, 1826; K. H. T. Kerndt, *Journ. prakt. Chem.*, (1), **42**. 113, 1847; E. F. Anthon, *ib.*, (1), **9**. 342, 1836; J. Brown, *Proc. Glasgow Phil. Soc.*, **2**. 180, 1848; *Phil. Mag.*, (3), **31**. 253, 1847; E. J. Chapman, *ib.*, (4), **6**. 120, 1853; W. A. Lampadius, *Schweigger's Journ.*, **31**. 254, 1821; F. von Kobell, *ib.*, **64**. 410, 1832; C. Friedheim, *Ueber die Konstitution der Metawolframsäure und ihrer Salze*, Freiburg, 16, 1882; F. C. Naumann, *Pogg. Ann.*, **34**. 373, 1835; E. Zettnow, *ib.*, **130**. 240, 1867; W. Florence, *Centr. Min.*, 725, 1903; E. Hussak, *ib.*, 723, 1903; H. Traube, *ib.*, 679, 1901; C. Hlawatsch, *ib.*, 422, 1905; *Ann. Hofmus. Wien*, **12**. 33, 1896; *Zeit. Kryst.*, **29**. 130, 1898; **31**. 1, 1899; **42**. 587, 1906; P. Niggli, *ib.*, **56**. 42, 1921; J. J. Saslawsky, *ib.*, **59**. 170, 1923; N. S. Manross, *Liebig's Ann.*, **81**. 243, 1852: **82**. 357, 1852; W. Lotz, *ib.*, **91**. 49, 1854; E. Cane, *Rend. Accad. Napoli*, (3), **32**. 83, 1926; H. C. Germs, *De thermische Analyse van Loodsulfaat, -chromaat, -molybdaat, en -wolframaat en van hun binaire Combinaties*, Groningen, 1917; F. M. Jäger and H. C. Germs, *Zeit. anorg. Chem.*, **119**. 161, 1921; G. Tammann, *ib.*, **149**. 21, 1925; **160**. 101, 1927; D. Balareff, *ib.*, **160**. 92, 1927; F. A. Henglein, *ib.*, **120**. 77, 1922; A. Rosenheim and F. Kohn, *ib.*, **69**. 251, 1911; W. Jander, *ib.*, **174**. 11, 1928; L. Michel, *Bull. Soc. Min.*, **2**. 142, 1879; *Recherches sur quelques tungstates, molybdates, séléniates, tellurates cristallisés*, Paris, 1889; W. Meyerhoffer, *Zeit. phys. Chem.*, **38**. 307, 1901; J. C. H. Mingaye, *Rec. Geol. Sur. New South Wales*, **9**. 171, 1916; A. T. Ullmann, *Journ. Roy. Soc. N.S.W.*, **46**. 186, 1912; C. D. Smith and L. A. Cotton, *ib.*, **46**. 207, 1912; F. Krantz, *Nature*, Sept. 12, advt., 1912; D. Lovisato, *Atti Accad. Lincei*, (5), **13**. ii, 43, 1904; F. Zambonini, *Riv. Min. Ital.*, **45**. 1, 1915; *Gazz. Chim. Ital.*, **50**. ii, 128, 1920; *Sulle soluzioni solide dei composti di calcio, stronzio, bario, e piombo con quelli delle " terre rare " e loro importanze per la mineralogia chimica*, Padova, 1915; *Atti Accad. Lincei*, (5), **22**. i, 519, 1913; F. de Carli, *ib.*, (6), **1**. 533, 1925; E. Artini, *Rend. Ist. Lombardo*, **38**. 373, 1905; *Riv. Min. Crist. Ital.*, **16**. 25, 1896; L. Kahlenberg and W. J. Trautmann, *Trans. Amer. Electrochem. Soc.*, **39**. 377, 1921; B. K. Emerson, *Bull. U.S. Geol. Sur.*, 126, 1895; E. S. Larsen, *ib.*, 679, 1921; E. F. Smith, *Chem. News*, **135**. 113, 129, 1927; E. F. Smith and R. H. Bradbury, *Bull. Soc. Chim.*, (3), **8**. 280, 1892; *Ber.*, **24**. 2930, 1891; D. Vorländer and H. Hempel, *ib.*, **60**. B, 845, 1927; E. Wartmann, *Mém. Sciences Genève*, (1), **12**. 1, 1853; L. Vegard and A. Refsum, *Norske Vid. Akad. Skr.*, 2, 1927.

[12] E. F. Smith and R. H. Bradbury, *Ber.*, **24**. 2930, 1891; F. Zambonini, *Gazz. Chim. Ital.*, **50**. ii, 128, 1920; J. Lefort, *Compt. Rend.*, **87**. 748, 1878; **88**. 798, 1879; C. W. Balke and E. F. Smith, *Journ. Amer. Chem. Soc.*, **25**. 1229, 1903.

[13] E. F. Smith, *Proc. Amer. Phil. Soc.*, **44**. 151, 1905.

[14] J. Lefort, *Ann. Chim. Phys.*, (5), **15**. 337, 1878; (5), **17**. 483, 1879; *Compt. Rend.*, **88**. 798, 1879; E. F. Smith and H. L. Dieck, *Zeit. anorg. Chem.*, **5**. 13, 1893; E. F. Smith, *ib.*, **15**. 151, 1893; W. Lotz, *Liebig's Ann.*, **91**. 66, 1854; W. Kantscheff, *Chem. Ztg.*, **36**. 199, 1912; *Journ. Russ. Phys. Chem. Soc.*, **46**. 729, 1914; S. Prakash and N. R. Dhar, *Journ. Indian Chem. Soc.*, **7**. 367, 1930.

[15] J. J. Berzelius, *Pogg. Ann.*, **6**. 384, 1826; C. F. Rammelsberg, *ib.*, **59**. 31, 1843; J. Lefort, *Compt. Rend.*, **87**. 749, 1878; *Ann. Chim. Phys.*, (5), **15**. 321, 1878; O. W. Gibbs, *Amer. Chem. Journ.*, **17**. 174, 1895; L. Fernandes, *Gazz. Chim. Ital.*, **56**. 655, 1926.

[16] E. F. Anthon, *Journ. prakt. Chem.*, (1), **9**. 339, 1836; A. Geuther and E. Forsberg, *Liebig's Ann.*, **120**. 273, 1861; E. Zettnow, *Pogg. Ann.*, **130**. 249, 1867; P. Groth and A. Arzruni, *ib.*, **149**. 236, 1873; A. Just, *Ber.*, **36**. 3619, 1903; A. Rogers and E. F. Smith, *Journ. Amer. Chem. Soc.*, **26**. 1475, 1904; A. Rosenheim, *Zeit. anorg. Chem.*, **96**. 139, 1916; A. Rosenheim and H. Schwer, *ib.*, **89**. 233, 1914; H. Schwer, *Ueber neunbasische Heteropolysäuren*, Berlin, 1914; E. K. Broch, *Zeit. phys. Chem.*, **1**. B, 406, 1928; *Norske Vid. Akad. Skr.*, 8, 1929; W. Jander, *Zeit. anorg. Chem.*, **191**. 171, 1930; **192**. 286, 295, 397, 1930.

[17] J. J. and F. de Elhuyar, *Análisis quimico del volfram y exámen de un nuovo metal que entra en su composicion*, Bascongada, 1783; *A Chemical Examination of Wolfram and Examination of a New Metal which enters into its Composition*, London, 1785; *Chemische Zerkleiderung des Wolframs*, Halle, 1786; *Mém. Acad. Toulouse*, **2**. 141, 1784; A. Weisbach, *Synopsis mineralogica*, Freiberg, 40, 1875; A. Breithaupt, *Vollstandige Charakteristik des Mineralsystems*, Dresden, 227, 1832; *Berg. Hütt. Ztg.*, **11**. 189, 1852; H. Credner, *ib.*, 24. 370, 1865; E. Riotte in H. Credner, *Berg. Hütt. Ztg.*, 24. 370, 1865; K. L. T. Liebe, *Neues Jahrb. Min.*, 652, 1863; O. Luedecke, *ib.*, 286, 1879; C. F. Rammelsberg, *Pogg. Ann.*, **77**. 246, 1849; **84**. 154, 1851; *Handbuch der Mineralchemie*, Leipzig, 309, 1868; 286, 1875; *Sitzber. Akad. Berlin*, 175, 1864; *Journ. prakt. Chem.*,

(1), **92**. 263, 1864 ; W. Beck and N. Teich, *Proc. Russ. Min. Soc.*, (2), **4**. 314, 1869 ; N. von Kulibin, *ib.*, (2), **3**. 1, 1868 ; P. von Jeremejeff, *ib.*, (2), **17**. 301, 1872 ; (2), **31**. 404, 1894 ; K. H. T. Kerndt, *Phil. Mag.*, (3), **31**. 253, 1847 ; *Journ. prakt. Chem.*, (1), **42**. 81, 1847 ; R. Schneider, *ib.*, (1), **49**. 322, 1850 ; T. Richardson, *Thomson's Records*, **1**. 449, 1835 ; *Journ. prakt. Chem.*, (1), **8**. 54, 1836 ; J. Lehmann, *ib.*, (1), **61**. 160, 1854 ; F. A. Genth, *The Minerals of North Carolina*, Washington, 1891 ; *Amer. Journ. Science, ib.*, (2), **28**. 253, 1857 ; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, 20, 1885 ; *Amer. Journ. Science*, (3), **27**. 357, 1884 ; C. H. Warren, *ib.*, (4), **11**. 372, 1901 ; A. J. Moses, *ib.*, (4), **20**. 281, 1905 ; S. L. Penfield, *ib.*, (3), **43**. 184, 1892 ; H. F. Keller, *Journ. Franklin Inst.*, **128**. 153, 1889 ; F. A. Bernoulli, *Pogg. Ann.*, **111**. 603, 1860 ; G. Rose, *ib.*, **64**. 171, 1845 ; P. Groth, *Zeit. deut. geol. Ges.*, **22**. 381, 1870 ; P. Groth and A. Arzruni, *Pogg. Ann.*, **149**. 237, 1873 ; F. von Schaffgotsch, *ib.*, **52**. 475, 1841 ; A. Petzholdt, *ib.*, **93**. 474, 1854 ; A. Carnot, *Compt. Rend.*, **79**. 637, 1874 ; P. Nicolardot, *ib.*, **144**. 859, 1907 ; A. de Gramont, *ib.*, **118**. 591, 746, 1894 ; T. L. Phipson, *ib.*, **65**. 419, 1867 ; I. Domeyko, *Ann. Mines*, (6), **16**. 537, 1869 ; A. des Cloizeaux, *Bull. Soc. Min.*, **5**. 105, 1882 ; *Ann. Chim. Phys.*, (3), **28**. 163, 1850 ; (4), **19**. 168, 1870 ; F. Bourion, *ib.*, (8), **21**. 103, 1910 ; J. J. Ebelmen, *Ann. Mines*, (4), **4**. 407, 1843 ; *Ann. Chim. Phys.*, (3), **8**. 505, 1843 ; L. N. Vauquelin, *ib.*, (2), **30**. 104, 261, 1825 ; V. H. Regnault, *ib.*, (3), **1**. 129, 1841 ; J. A. Krenner, *Tschermak's Mitt.*, (1), **5**. 9, 1875 ; G. Seligmann, *Zeit. Kryst.*, **11**. 347, 1886 ; W. H. Miller, *Introduction to Mineralogy*, London, 473, 1852 ; A. Liversidge, *The Minerals of New South Wales*, Sydney, 85, 1888 ; R. Tronquoy, *Bull. Soc. Min.*, **36**. 113, 1913 ; J. J. Bravo, *Arch. Asoc. Peruana Cienciat.*, **1**. 144, 1922 ; G. Bodenbender, *Zeit. prakt. Geol.*, **12**. 409, 1904 ; P. P. Pilipenko, *Bull. Tomsk. Univ.*, 63, 1915 E. T. Wherry, *Proc. U.S. Nat. Museum*, **47**. 501, 1914 ; *Amer. Min.*, **10**. 28, 1925 ; P. Geijer, *Geol. För. Förh. Stockholm*, **45**. 434, 1923 ; W. H. Hobbs, *Amer. Geol.*, **36**. 179, 1905 ; O. B. Böggild, *Mineralogia Groenlandica*, Copenhagen, 180, 1905 ; *Medd. Grönland*, **32**. 1, 1907 ; C. Anderson, *Rec. Australian Museum*, **5**. 303, 1904 ; A. S. Eakle, *Bull. Univ. Cal. Geol. Dept.*, **7**. 18, 1912 ; C. Granell, *Boll. Soc. Esp. Hist. Nat.*, **9**. 81, 1909 ; A. M. Findlayson, *Geol. Mag.*, (5), **7**. 19, 1910 ; H. Winter, *Ueber Vorkommen und Reindarstellung des Scandiums*, Berlin, 1911 ; R. J. Meyer and H. Winter, *Zeit. anorg. Chem.*, **67**. 398, 1910 ; W. Hempel, *ib.*, **3**. 193, 1893 ; L. Weiss, *ib.*, **65**. 286, 1910 ; W. L. Walker, *Econ. Geol.*, **6**. 396, 1911 ; T. L. Walker, *Canadian Dept. Mines*, 38, 1909 ; J. D. Irving, *Trans. Amer. Inst. Min. Eng.*, **31**. 683, 1901 ; E. F. Smith, *Journ. Amer. Chem. Soc.*, **20**. 289, 1898 ; E. A. Atkinson, *ib.*, **20**. 797, 1898 ; G. Eberhard, *Sitzber. Akad. Berlin*, 404, 1910 ; *Zeit. anorg. Chem.*, **45**. 374, 1905 ; *Chem. News*, **99**. 30, 1909 ; **102**. 211, 1910 ; V. Goldschmidt, *Krystallographische Winkeltabellen*, Berlin, 366, 1897 ; F. Sandberger, *Sitzber. Acad. München*, 423, 1888 ; A. Damour, *Bull. Soc. Geol.*, (2), **5**. 108, 1848 ; J. B. Ekeley, *Min. World*, **30**. 280, 1909 ; *Univ. Colorado Min. Studies*, **6**. 95, 1909 ; G. J. Pöpplein, *Mining Mag.*, **2**. 359, 1859 ; G. Weidinger, *Zeit. Pharm.*, **7**. 71, 1855 ; T. Thomson, *Outlines of Mineralogy, Geology, and Mineral Analysis*, London, **1**. 487, 1836 ; F. Hoppe-Seyler, *Liebig's Ann.*, **140**. 247, 1866 ; B. Bavink, *Beiträge zur Kenntnis der magnetischen Influenz in Krystallen*, Stuttgart, 1904 ; F. L. Hess, *Bull. U.S. Geol. Sur.*, 583, 1914 ; 652, 1917 ; (I am indebted to Mr. F. L. Hess for permission to use Figs. 47 to 49 from Bull. 652) ; W. T. Schaller, *ib.*, 583, 1914 ; E. S. Larsen, *ib.*, 679, 1921 ; Wolf Tongue Milling Co., *ib.*, 652, 1917 ; K. von Fritsch, *Zeit. Naturwiss. Halle*, **3**. 864, 1878 ; J. J. Berzelius, *Schweigger's Journ.*, **16**. 476, 1816 ; F. N. Guild, *The Mineralogy of Arizona*, Easton, Pa., 92, 1910 ; F. Mohs, *Gründriss der Mineralogie*, Dresden, 1922 ; A. F. Gehlen, *Schweigger's Journ.*, **6**. 257, 1812 ; L. Sipöcz, *Ber.*, **19**. 95, 1896 ; *Tschermak's Mitt.*, (2), **16**. 256, 1896 ; A. Geuther and E. Forsberg, *Liebig's Ann.*, **120**. 273, 1861 ; H. Kopp, *Liebig's Ann. Suppl.*, **3**. 289, 1865 ; G. Lindner, *Die Abhangigkeit der specifischen Wärme fester Körper von der Temperatur*, Erlangen, 1903 ; E. Wartmann, *Mém. Sciences Genève*, (1), **12**. 1, 1853 ; F. Beijerinck, *Neues Jahrb. Min. B.B.*, **11**. 403, 1897 ; J. J. Runner, *Mining Scient. Press.*, **133**. 11, 1916 ; B. Setlik, *Chem. Ztg.*, **13**. 1474, 1889 ; C. A. Burghardt, *Chem. News*, **61**. 260, 1890 ; W. B. Giles, *ib.*, **76**. 139, 1897 ; E. Bertrand, *Bull. Soc. Min.*, **5**. 90, 1882 ; M. Kosaki, *Bull. Inst. Phys. Chem. Research, Tokyo*, **7**. 540, 1928 ; K. Jimbo, *Journ. Tokyo Coll. Science*, **11**. 213, 1899 ; L. J. Spencer, *Min. Mag.*, **14**. 334, 1905 ; H. S. Lukens, *Journ. Amer. Chem. Soc.*, **35**. 1470, 1913 ; W. P. Headden, *Proc. Colorado Scient. Soc.*, **8**. 175, 1906 ; R. Helmhacker, *Eng. Min. Journ.*, **62**. 154, 1896 ; W. E. Greenawalt, *ib.*, **83**. 951, 1907 ; T. S. Hunt, *Canadian Journ.*, (2), **5**. 303, 1860 ; A. W. G. Bleeck, *Indian Geol. Sur. Records*, **43**. i, 67, 1913 ; L. L. Fermor, *ib.*, **36**. iv, 309, 1908 ; O. J. Steinhart, *Min. Ind.*, **17**. 830, 1909 ; L. C. Ball, *Queensland Govt., Min. Journ.*, **14**. 70, 1913 ; J. E. Carne, *Min. Resources N.S.W. Geol. Sur.*, 15, 1912 ; *The Tungsten Mining Industry of New South Wales*, Sydney, 1912 ; R. D. George, *Rep. Colorado Geol. Sur.*, **1**. 43, 1909 ; T. Wada, *Minerals of Japan*, Tokyo, 77, 1904 ; A. Jahn, *Mitt. Vogtl. Ges. Naturf. Plauen*, 3, 1926 ; C. Doelter, *Zeit. anorg. Chem.*, **67**. 387, 1910 ; F. Machatschky, *Zeit. Kryst.*, **67**. 163, 1928 ; A. Ambronn, *Methodes de la géophysique appliquée*, Dresden, 1926 ; G. Grenet, *Ann. Physique*, (10), 13. 263, 1930 ; E. Zettnow, *Pogg. Ann.*, **130**. 249, 1867 ; E. K. Broch, *Norske Vid. Akad. Skr.*, 8, 1929 ; I. Pargo and A. Arango, *Anal. Fis. Quim.*, **28**. 905, 1930 ; F. R. van Horn, *Amer. Min.*, 15. 461, 1930 ; D. J. Fisher, *ib.*, **15**. 104, 1930 ; P. Pondal and J. Vasquez-Garriga, *Arq. Sem. Estudos Galegos*, **3**. 5, 1929 ; A. H. Low, *Bull. U.S. Geol. Sur.*, 20, 1885 ; *Amer. Journ. Science*, (3), 27. 358, 1886.

[18] G. Tammann, *Zeit. anorg. Chem.*, **149**. 21, 1925 ; **160**. 101, 1927 ; A. Rosenheim and H. Schwer, *ib.*, **89**. 229, 1914 ; W. Lotz, *Liebig's Ann.*, **91**. 49, 1854 ; A. Geuther and E. Forsberg, *ib.*, **120**. 270, 1861 ; E. S. Larsen, *Bull. U.S. Geol. Sur.*, 679, 1921 ; H. Debray, *Compt.*

Rend., **55**. 287, 1862 ; A. Laurent, *ib.*, **31**. 392, 1850 ; J. Lefort, *ib.*, **87**. 748, 1879 ; *Ann. Chim. Phys.*, (5), **15**. 321, 1879 ; E. F. Anthon, *Journ. prakt. Chem.*, (1), **9**. 341, 1836 ; E. Zettnow, *Pogg. Ann.*, **130**. 30, 1867 ; W. T. Schaller, *Amer. Journ. Science*, (4), **32**. 161, 1911 ; S. Prakash and N. R. Dhar, *Journ. Indian Chem. Soc.*, **6**. 587, 1929 ; **7**. 367, 1930 ; E. K. Broch, *Norske Vid. Akad. Skr.*, 8, 1929 ; D. Balareff, *Zeit. anorg. Chem.*, **153**. 184, 1926.

[19] F. de Carli, *Atti Accad. Lincei*, (6), **1**. 533, 1925 ; H. Schultze, *Ueber die Darstellung krystallisirter Verbindungen insbesondere über einige krystallisirte molybdänsaure und wolframsäure Salze*, Göttingen, 1862 ; *Liebig's Ann.*, **126**. 49, 1863 ; H. O. Schulze, *Journ. prakt. Chem.*, (2), **21**. 441, 1880 ; E. Zettnow, *Pogg. Ann.*, **130**. 252, 1867 ; E. K. Broch, *Zeit. phys. Chem.*, **1**. B, 409, 1928 ; *Norske Vid. Akad. Skr.*, 8, 1929 ; E. F. Anthon, *Journ. prakt. Chem.*, (1), **9**. 344, 1836 ; A. Carnot, *Compt. Rend.*, **109**. 147, 1889 ; J. Lefort, *ib.*, **87**. 748, 1878 ; **88**. 798, 1879 ; F. W. Clarke and J. L. Davis, *Amer. Journ. Science*, (3), **14**. 281, 1877 ; A. Rogers and E. F. Smith, *Journ. Amer. Chem. Soc.*, **26**. 1474, 1904 ; E. F. Smith and R. H. Bradbury, *Ber.*, **24**. 2930, 1891 ; G. L. Clark, *Amer. Journ. Science*, (5), **7**. 1, 1924 ; W. Jander, *Zeit. anorg. Chem.*, **191**. 171, 1930 ; **192**. 286, 295, 1930.

[20] O. W. Gibbs, *Amer. Journ. Science*, (3), **14**. 61, 1877 ; *Amer. Chem. Journ.*. **17**. 77, 1895 ; *Proc. Amer. Acad.*, **30**. 255, 1894 ; *Ber.*, **10**. 1384, 1877 ; A. Rosenheim, *ib.*, **24**. 2397, 1891.

§ 13. The Ditungstates and Tritungstates

The conditions of equilibrium of **lithium ditungstate,** $Li_2W_2O_7$, according to J. A. M. van Liempt,[1] and F. Hoermann are shown in Fig. 25. The crystals are probably rhombic, and the compound melts at 745°, and has a transition point at 687°. G. von Knorre melted a mixture of a mol of sodium carbonate and 2 mols of tungsten trioxide and obtained, on cooling, a mass of acicular—probably rhombic—crystals of **sodium ditungstate,** $Na_2O.2WO_3$. It dissolves completely when heated for some hours with water at 130°–150°, and the alkaline soln. does not crystallize ; it contains sodium tungstate and metatungstate. I. Traube found the drop weight of the molten salt to be 189 when that of water at 0° is 100. F. Hoermann, and J. A. M. van Liempt studied the conditions of equilibrium, Fig. 25 ; the compound has a m.p. of 738°, and a transition temp. of 747°. V. I. Spitzin and L. Kaschtanoff found the reaction with hydrogen chloride is to form the oxydichloride and normal tungstate which reacts as previously indicated. C. Scheibler studied the action of phosphoric acid on the tungstate ; and J. Lefort obtained quinine ditungstate by the action of a soln. of quinine. J. Lefort reported the *hexahydrate* to be formed in prismatic crystals when a cold, sat. soln. of sodium tungstate is mixed with acetic acid—if oxalic acid is used, the product is contaminated with sodium oxalate. The salt is stable in air ; it melts in its own water of crystallization ; and 100 parts of water at 15° dissolve 13 parts of the salt. G. von Knorre could not prepare this salt, but always obtained the paratungstate instead. C. Friedheim reported that prismatic crystals of the *dodecahydrate* separate from the mother-liquor obtained in preparing sodium vanadatotungstate. It is decomposed by water into normal tungstate and paratungstate. For the observations of V. I. Spitzin, and others, on the reduction of the ditungstates, *vide supra*, sodium bronzes. A. Riche fused an equimolar mixture of tungsten trioxide and potassium tungstate, poured the mass on a cold marble slab, and obtained a colourless crystalline mass. E. F. Anthon made a similar experiment. According to J. Lefort, if acetic or oxalic acid is gradually poured into a cold, conc. soln. of potassium tungstate, a white, curdy precipitate of **potassium ditungstate,** $K_2O.2WO_3.2H_2O$, is formed. 100 parts of water at 15° dissolve 8 parts of the *dihydrate*. If the soln. in boiling water be cooled, the *trihydrate* separates out. 100 parts of water dissolve 2 to 3 parts of the salt. M. Amadori's thermal analysis showed that a potassium ditungstate exists. As in the case of sodium ditungstate, G. von Knorre could not verify J. Lefort's observations, since the paratungstate was always formed. O. W. Gibbs, C. Gonzales, and E. F. Smith were unable to confirm J. Lefort's observation—*vide infra*, the decatungstates. J. A. M. van Liempt's study of the system $K_2WO_4.WO_3$ does not show the existence of any stable ditungstate, Fig. 33.

E. F. Anthon said that if a soln. of a copper salt is treated with an alkali ditungstate, a pale green precipitate of **copper ditungstate,** $CuO.2WO_3.4H_2O$, is formed.

It is decomposed by heat, with the loss of water. It is then brown. The salt is soluble in aq. ammonia, and is decomposed by nitric acid. Many of the ditungstates reported by the early workers appear to have been paratungstates. J. Lefort obtained anhydrous **calcium ditungstate**, $CaO.2WO_3$, as a white precipitate by treating a soln. of calcium acetate with sodium ditungstate at 15°. 100 parts of water dissolve 0·2 part of the salt. If the mother-liquor be evaporated, or if the precipitate be boiled with water, white plates of the *trihydrate* are formed. At 15°, 100 parts of water dissolve 3·3 parts of the salt. E. F. Anthon obtained what he regarded as **strontium ditungstate,** $SrO.2WO_3.4H_2O$, by double decomposition; and J. Lefort obtained a *trihydrate* as a white precipitate by the action of a soln. of sodium ditungstate on one of strontium acetate. E. F. Anthon's product was insoluble in cold water, but soluble in hot phosphoric and oxalic acids. J. Lefort prepared **barium ditungstate,** $BaO.2WO_3.H_2O$, as in the case of the calcium salt. It is more soluble in water than normal barium tungstate. J. Lefort prepared **magnesium ditungstate;** $MgO.2WO_3.8H_2O$, by warming a mixture of magnesium hydroxide with an excess of tungstic acid, and a little water on a sand-bath for several hours' replacing the water lost by evaporation from time to time. Prismatic crystals are formed; at 15°, 100 parts of water dissolve one part of salt. An aq. soln. of magnesium tritungstate deposits a basic salt, $3MgO.2WO_3.4H_2O$, after some hours. J. Lefort obtained **zinc ditungstate,** $ZnO.2WO_3.3H_2O$, in acicular crystals, by concentrating a mixed soln. of a zinc salt and sodium ditungstate; 100 parts of water at 15° dissolve 10 parts of the salt. E. F. Anthon treated an excess of a boiling soln. of mercuric chloride with sodium tungstate and obtained a white insoluble precipitate of **mercuric ditungstate,** $HgO.2WO_3$, which is decomposed by soda-lye to form red mercuric oxide.

J. Lefort mixed soln. of lead acetate and sodium ditungstate and obtained **lead ditungstate,** $PbO.2WO_3.2H_2O$, as a white precipitate which loses its water when heated; it melts at a red-heat; and at 15°, 100 parts of water dissolve 1·25 parts of salt. J. Lefort mixed soln. of bismuth acetate and sodium tritungstate in the presence of alcohol, and obtained **bismuth ditungstate,** $Bi_2(W_2O_7)_3.8H_2O$, as a white precipitate.

E. F. Anthon obtained **ferrous ditungstate,** $FeO.2WO_3.2H_2O$, as a brick-red or brown precipitate by treating a soln. of a ferrous salt with an alkali ditungstate —J. J. Ebelmen used ammonium ditungstate. The salt is not soluble in water, but it dissolves in hot oxalic or phosphoric acid; dil. hydrochloric acid extracts the iron, but with the conc. acid some ferrous iron is oxidized and some blue tungsten oxide is formed. Cold alkali-lye extracts tungsten trioxide. E. F. Anthon obtained a reddish-brown precipitate of **cobalt ditungstate,** $CoO.2WO_3.3H_2O$, by treating a cobalt salt soln. with sodium ditungstate. The precipitate is insoluble in water, sparingly soluble in oxalic acid, and soluble in warm phosphoric acid, acetic acid, and aq. ammonia. E. F. Anthon also reported **nickel ditungstate,** $NiO.2WO_3.4H_2O$. As indicated above, many of these ditungstates are now thought to be paratungstates.

J. C. G. de Marignac [2] obtained normal ammonium tungstate by evaporating over quicklime a soln. of hydrated tungstic acid in aq. ammonia; but, on one occasion he obtained **ammonium tritungstate,** $4(NH_4)_2O.3WO_3.3H_2O$, in indistinct crystals which dissolve in aq. ammonia, forming the normal salt; the aq. soln. soon deposits crystals of the normal salt. E. T. Allen and V. H. Gottschalk added hydroxylamine hydrochloride to a soln. of sodium tungstate, and obtained white crystals of **hydroxylamine tritungstate,** $4(NH_2OH).3WO_3.3H_2O$. When dry, the colour is pale yellow. The salt decomposes vigorously when heated; and it is freely soluble in water.

C. Scheibler obtained **sodium tritungstate,** $2Na_2O.3WO_3.7H_2O$, as a decomposition product of sodium paratungstate, for when that salt is heated to redness, and when cold, extracted with water, a tetratungstate remains undissolved. The aq. extract, on evaporation, furnishes first a crop of crystals of paratungstate, and then a crop of the tritungstate. This salt melts at a dull red-heat; it is freely soluble in water; and the aq. soln. reacts alkaline. J. Lefort studied the action of quinine on the alkali tritungstates. J. Lefort obtained the tritungstate, $Na_2O.3WO_3.4H_2O$, by adding a conc. soln. of sodium ditungstate, drop by drop, to boiling acetic acid. The white, gelatinous precipitate dissolves in its own weight of water, and the aq. soln. when evaporated over quicklime and sulphuric acid, furnishes prismatic crystals. According to J. Lefort, if a conc., aq. soln. of normal potassium tungstate is poured into boiling conc. acetic acid, **potassium tritungstate,** $K_2O.3WO_3.2H_2O$, is formed; but if the soln. is not filtered at once, the metatungstate is formed. The white precipitate is soluble in 5 or 6 times its weight of water at 15°. The salt is obtained in fine needles and prisms when the aq. soln. is evaporated over quicklime, and conc. sulphuric acid. If the aq. soln. is boiled a long time, the ditungstate is formed which separates in scaly crystals, while the normal tungstate remains in soln. If boiled with acetic acid, for a long time, the metatungstate is produced. M. Amadori's thermal analysis showed that a tritungstate of potassium can exist; and F. Hoermann's equilibrium diagram, Fig. 35, shows that potassium tritungstate has an incongruent m.p. at 660°.

J. Lefort was unable to prepare **copper tritungstate,** $CuO.3WO_3.nH_2O$, by adding alcohol to a soln. of aq. proportions of copper acetate and sodium tritungstate. By mixing soln. of calcium acetate and sodium tritungstate, J. Lefort obtained a white, curdy precipitate of **calcium tritungstate,** $CaO.3WO_3.6H_2O$, soluble in cold water; and similarly with **strontium tritungstate,** $SrO.3WO_3.5H_2O$; and with **barium tritungstate,** $BaO.3WO_3.4H_2O$. At 15°, 100 parts of water dissolve 0·33 part of the salt. The *tetrahydrate* is not decomposed by cold water, but with boiling water, the ditungstate and tetratungstate are formed. C. Scheibler obtained the *hexahydrate* as a white powder by the action of cold water on barium metatungstate. J. Lefort obtained white **magnesium tritungstate,** $MgO.3WO_3.4H_2O$, by pouring a mixed soln. of magnesium acetate and sodium tritungstate into alcohol. The salt is soluble in water, and after the soln. has stood for some hours, deposits a basic salt, $3MgO.2WO_3.4H_2O$. O. W. Gibbs obtained **zinc tritungstate,** $ZnO.3WO_3.5H_2O$, which he represented by $2ZnO.6WO_3.10H_2O$, by heating a soln. of sodium pentatungstate mixed with zinc sulphate. The soln. deposits aggregates of acicular crystals which are almost insoluble in boiling water, but soluble in soln. of zinc sulphate, and sodium tungstate. J. Lefort obtained **cadmium tritungstate,** $CdO.3WO_3.4H_2O$, as a white precipitate by adding alcohol to a mixed soln. of cadmium acetate and sodium tritungstate, and allowing the liquid to stand. J. Lefort obtained **mercurous tritungstate,** $2Hg_2O.3WO_3.8H_2O$, by dissolving mercurous nitrate, by the aid of glycerol, in water, and pouring the filtered soln. into a conc. soln. of sodium ditungstate. The pale yellow, stable precipitate loses water when warmed; 100 parts of water dissolve one part of the salt; but he was unable to obtain a tritungstate by pouring the soln. of mercurous nitrate in glycerol into a soln. of sodium tritungstate. The white precipitate first formed immediately blackened owing to the separation of mercury. E. F. Anthon treated a soln. of mercuric nitrate with normal sodium tungstate and obtained **mercuric tritungstate,** $2HgO.3WO_3$, as a white, insoluble powder. J. Lefort obtained the *heptahydrate,* $HgO.3WO_3.7H_2O$, by pouring a soln. of 2 eq. of sodium ditungstate into a sat. soln. of an eq. of mercuric chloride, and allowing the soln. to crystallize. The prismatic crystals, when heated, lose water while retaining their external crystalline form. At 15°, 100 parts of water dissolve 0·83 part of salt. J. Lefort mixed soln. of lead acetate and sodium tritungstate in excess, and obtained **lead tritungstate,** $PbO.3WO_3.2H_2O$, as a white powder, which is very sparingly soluble in water with partial decomposition.

C. F. Rammelsberg added ordinary ammonium tungstate to an aq. soln. of uranium tetrachloride, and obtained **uranium tritungstate** as a brownish-green precipitate, $(UO_2)3WO_3.6H_2O$. Boiling potash-lye extracts all the tungsten trioxide from the moist precipitate, but only part if the precipitate has been dried; and similarly with aq. ammonia. Nitric acid extracts the uranium, and leaves the tungsten trioxide. This compound is used in the manufacture of fluorescent screens for X-ray work. J. Lefort prepared **uranyl tritungstate,** $UO_2.W_3O_{10}.5H_2O$, from a soln. of uranium acetate and sodium tritungstate.

J. Lefort obtained **manganous tritungstate,** $MnO.3WO_3.5H_2O$ (dried at 100°), by adding alcohol to a mixed soln. of manganous acetate and sodium tritungstate. The precipitate is decomposed by cold or hot water forming di- and tetra-tungstates. J. Lefort prepared **cobalt tritungstate,** $CoO.3WO_3.4H_2O$, in the case of manganous tritungstate. The rose-red precipitate is decomposed by water. Greenish-white **nickel tritungstate,** $NiO.3WO_3.4H_2O$, was similarly obtained.

References.

[1] G. von Knorre, *Journ. prakt. Chem.*, (2), **27**. 49, 1883 ; C. Scheibler, *Zeit. Naturwiss. Halle*, **40**. 298, 1872 ; J. Lefort, *Compt. Rend.*, **82**. 1182, 1876 ; **92**. 1461, 1881 ; *Journ. Chim. Pharm.*, (5), **4**. 221, 1881 ; *Ann. Chim. Phys.*, (5), **9**. 96, 1876 ; (5), **15**. 327, 1878 ; C. Friedheim, *Ber.*, **23**. 1509, 1890 ; I. Traube, *ib.*, **24**. 3074, 1891 ; E. F. Anthon, *Repert. Pharm.*, **76**. 349, 1836 ; *Journ. prakt. Chem.*, (1), **8**. 399, 1836 ; (1), **9**. 337, 1826 ; A. Riche, *Recherches sur le tungstène et ses composés*, Paris, 1857 ; (3), **50**. 15, 1857 ; J. J. Ebelmen, *Compt. Rend.*, **17**. 1198, 1843 ; J. A. M. van Liempt, *Zeit. anorg. Chem.*, **143**. 285, 1925 ; F. Hoermann, *ib.*, **177**. 145, 1928 ; V. I. Spitzin, *Journ. Russ. Phys. Chem. Soc.*, **58**. 474, 1926 ; *Zeit. Phys. Chem.*, **148**. 69, 1925 ; V. I. Spitzin and L. Kaschtanoff, *ib.*, **157**. 141, 1926 ; M. Amadori, *Atti Ist. Veneto*, **72**. ii, 893, 1916 ; O. W. Gibbs, *Proc. Amer. Acad.*, **15**. 1, 1879 ; *Amer. Chem. Journ.*, **1**. 2, 218, 1879 ; C. Gonzalez, *Journ. prakt. Chem.*, (2), **36**. 44, 1887 ; E. F. Smith, *Chem. News*, **129**. 198, 207, 224, 240, 257, 286, 1924 ; *Journ. Amer. Chem. Soc.*, **44**. 2027, 1922.

[2] J. C. G. de Marignac, *Ann. Chim. Phys.*, (3), **69**. 23, 1863 ; E. T. Allen and V. H. Gottschalk, *Amer. Chem. Journ.*, **27**. 328, 1902 ; C. Scheibler, *Phys. Rev.*, (1), **80**. 204, 1860 ; *Journ. prakt. Chem.*, (1), **83**. 273, 1861 ; *Chem. News*, **6**. 181, 1862 ; *Sitzber. Akad. Berlin*, 208, 1860 ; *De wolframiatibus*, Königsberg, 1861 ; J. Lefort, *Compt. Rend.*, **82**. 1182, 1876 ; **88**. 798, 1879 ; *Ann. Chim. Phys.*, (5), **9**. 103, 1876 ; (5), **15**. 355, 1878 ; (5), **17**. 470, 1879 ; *Journ. Pharm. Chim.*, (5), **4**. 221, 1881 ; O. W. Gibbs, *Proc. Amer. Acad.*, **15**. 1, 1879 ; *Amer. Chem. Journ.*, **1**. 2, 218, 1879 ; E. F. Anthon, *Repert. Pharm.*, **76**. 349, 1836 ; *Journ. prakt. Chem.*, (1), **8**. 399, 1836 ; (1), **9**. 337, 1836 ; F. A. Bernoulli, *Pogg. Ann.*, **111**. 608, 1860 ; C. F. Rammelsberg, *ib.*, **59**. 31, 1843 ; W. Lotz, *Liebig's Ann.*, **91**. 49, 1854 ; M. Amadori, *Atti Ist. Veneto*, **72**. ii, 893, 1916 ; J. Hoermann, *Zeit. anorg. Chem.*, **177**. 145, 1928.

§ 14. The Paratungstates

> The alkali tungstates are numerous and unusually complex. Salts of essentially different formulæ approach so closely in percentage composition, that the differences lie very near the unavoidable errors of analysis. The analyses are hardly sufficiently close to decide the question upon purely analytical grounds.—O. W. Gibbs.

The so-called paratungstates are, in the literature, represented by the formula $3R_2O.7WO_3.nH_2O$, or by $5R_2O.12WO_3.nH_2O$—*vide supra*, paratungstic acid. A. Rosenheim[1] employed the co-ordinate formula $R_5H_5[H_2(WO_4)_6].nH_2O$. The usual product of the action of tungstic acid on aq. ammonia is **ammonium paratungstate,** $5(NH_4)_2O.12WO_3.11H_2O$, or $3(NH_4)_2O.7WO_3.6H_2O$, or $(NH_4)_5H_5[H_2(WO_4)_6]H_2O$. Thus, by concentrating an ammoniacal soln. of normal ammonium tungstate, or a soln. of tungstic acid in aq. ammonia, T. M. Taylor, W. Lotz, E. F. Anthon, and J. C. G. de Marignac obtained crystals of this salt. L. A. Hallopeau obtained it from a soln. of paratungstic acid neutralized by ammonia ; and E. Schaefer, by the electrolysis of a soln. of ammonium tungstate in a compartment cell—*vide infra*, sodium paratungstate. For C. Friedheim and R. Meyer's process for preparing the salt free from molybdenum, *vide infra*, sodium paratungstate. T. M. Taylor observed that a hot soln. furnishes needles of the *pentahydrate*, but, if the soln. is just warm, plates of the *henahydrate* are produced. According to J. C. G. de Marignac, the pentahydrate forms monoclinic prisms with the axial ratios $a:b:c=1\cdot0442:1:0\cdot7871$, and $\beta=109°\ 50'$. Twinning occurs about the (001)-plane. The salt loses 2·15 per cent. of water at 100° ; and ammonia begins to come off at 60°. The hot aq. soln. deposits crystals of the pentatungstate. According to O. W. Gibbs, a soln. of commercial ammonium tungstate in aq.

ammonia, when filtered, and treated with acetic acid, furnishes crystals of the *hexahydrate*, $5(NH_4)_2O.12WO_3.6H_2O$; A. Rosenheim and A. Wolff showed that the salt forms both the henahydrate and the *heptahydrate—vide infra.*

The henahydrate was analyzed by J. C. G. de Marignac, W. Lotz, C. Scheibler, A. Riche, E. Wegelin, J. J. Berzelius, E. F. Anthon, L. A. Hallopeau, A. Laurent, E. Schaefer, and A. Pinagel. According to A. Laurent, the salt is dimorphous, and, added E. F. Anthon, needles are obtained if slowly crystallized, and plates if rapidly crystallized; while A. Riche said that needles are deposited from a soln. at 50°–60°; and plates from a cold soln.; and E. Zettnow, that a warm soln. furnishes scaly crystals and a cold soln., prisms. According to J. C. G. de Marignac, the needles are pseudorhombic with the axial ratios $a:b:c=0·7995:1:0·4582$, and K. H. T. Kerndt added that the crystals are complex twinned forms of monoclinic plates. The crystals were also discussed by J. Schabus. J. C. G. de Marignac said that the plates are triclinic pinacoids with the axial ratios $a:b:c=0·9785:1:0·12154$, and $\alpha=65° 47'$, $\beta=117° 33'$, and $\gamma=119° 2'$. J. J. and F. de Elhuyar said that the crystals are stable in air, but they cannot be dehydrated without the loss of ammonia. According to A. Riche, W. Lotz, and J. C. G. de Marignac, the acicular form at 100° loses from 3·23 to 3·87 per cent. of water; and the tabular form 3·80 to 4·72 per cent. J. J. and F. de Elhuyar found that at a red-heat the salt is decomposed giving off water, ammonia, and nitrogen, and leaving behind the blue oxide or, if air be present, tungsten trioxide —as a pseudomorph of the tungstate (E. F. Anthon). T. M. Taylor found that at 100°, the acicular crystals lose 6 mols. of water; and inferred that the remaining 5 mols. are more closely associated in the molecule; and from the easy transformation of the para- into the meta-tungstate it is assumed that the 4 mols. of ammonia in the para-salt are differently combined in the molecule. If the henahydrate is deposited from a warm soln., continuously stirred, W. Lotz said that it is only sparingly soluble in water. E. F. Anthon found that 100 parts of cold water dissolve 3·6 to 4·0 parts of the salt; W. Lotz, 3·83 parts at 10·7°, and 1·69 parts at 100°; A. Riche, 3·003 parts in the cold, and 10·7 parts at 100°; and J. C. G. de Marignac, 2·63 to 4·54 parts at 15° to 18°. A. Rosenheim and A. Wolff found the solubility of the ammonium salt, S grms. of $5(NH_4)_2O.12WO_3$ in 100 grms. of soln., to be:

	17°	25°	35°	49°	52°	62°	70°
S . .	1·064	1·586	2·424	4·341	3·280	6·145	7·971
	11-hydrate				7-hydrate		

—*vide* the normal tungstate for its existence in aq. soln. W. Lotz added that the salt loses ammonia in boiling water, forming the more soluble metatungstate, and J. C. G. de Marignac also noted that the salt gradually changes in aq. soln. B. Kellner observed that the soln. of the salt in hydrogen dioxide is yellow, and when dried, it leaves an amorphous mass. E. F. Smith observed that aniline hydrochloride gives no precipitate with sodium and ammonium tungstates and meta-tungstates, but gives one with the paratungstate before, not after, the soln. is boiled. This shows that boiling water hydrolyzes the paratungstate into one of the other salts. According to T. M. Taylor, if dry ammonia, at about 14 mm. press., is passed over the acicular crystals, at 100° to 250°, about 9 mols. of water are given off; and at 100°–160° ammonia is absorbed to the extent of 3·2 mols. at 130°, but the actual amount varies with the temp. At 250°, the colloidal salt is formed containing tungsten trioxide. The composition of the product, assuming that a common nucleus, $NH_4OH.2WO_3$, is present, can be represented by the mol. ratios: $(NH_4OH.2WO_3):NH_4OH:NH_3$ at 100° is $6:1:4$; at 110°–120°, $6:1:5$; at 130°–140°, $6:1:6$; at 160°, $6:2:2$; at 200°, $6:2:1$; and at 250°, $4(NH_4OH.2WO_3).4WO_3.4NH_3$. E. F. Anthon found the salt to be insoluble in alcohol. D. Klein studied the action of boric acid on the salt. A. Laurent, and J. C. G. de Marignac evaporated a soln. of ammonium paratungstate mixed with a little nitric acid, or a soln. of ammonium paratungstate mixed with an excess of ammonium nitrate, and obtained hexagonal, prismatic crystals of **ammonium nitratometatungstate,** $NH_4NO_3.2(NH_4)_2W_4O_{13}.4H_2O$. The salt loses half its water at 100° ; and when heated, decrepitates, and decomposes without melting.

C. Scheibler prepared **lithium paratungstate,** $5Li_2O.12WO_3.33H_2O$, or $3Li_2O.7WO_3.19H_2O$, by adding tungstic acid to a soln. of lithium carbonate until the mixture is neutral to litmus ; and evaporating slowly over conc. sulphuric acid. The rhombic plates or prisms are stable in air, and the salt is more soluble in water than the corresponding sodium or potassium salt. The ordinary *sodium tungstate* of commerce is **sodium paratungstate,** $5Na_2O.12WO_3.mH_2O$, $3Na_2O.7WO_3.nH_2O$. F. Wöhler, and F. J. Malaguti prepared a salt with the composition $Na_2O : WO_3 = 3 : 7$ by fusing sodium tungstate with the required proportion of tungsten trioxide. The hydrated salt is manufactured by fusing wolframite with soda-ash, lixiviating the product with water, nearly neutralizing the boiling soln. with hydrochloric acid, and crystallizing—*vide supra*, the extraction of tungsten. Aq. soln. of the salt were obtained by E. F. Anthon by saturating a soln. of sodium hydroxide, carbonate, or tungstate with tungstic acid ; by C. Scheibler, O. W. Gibbs, G. von Knorre, and C. Gonzalez, by treating a boiling soln. of sodium tungstate with hydrochloric acid until it is faintly acid to litmus —C. Friedheim and R. Meyer recommended the process for preparing the salt free from molybdenum previously described in connection with the extraction of tungsten ; by V. Forcher, by saturating an aq. soln. of normal sodium tungstate with carbon dioxide ; by G. von Knorre, by mixing soln. of 5·8 grms. of $Na_2O.4WO_3.10H_2O$ and of 2 grms. of $Na_2O.WO_3.2H_2O$; and by E. Schaefer, by the electrolysis of a soln. of sodium tungstate in a compartment cell. The current acts by removing sodium hydroxide from the normal tungstate. A. Lottermoser thus described the process :

> A soln. of 51 grms. of dihydrated normal sodium tungstate in 200 c.c. of water is placed in a 250 c.c. porous pot which stands in a beaker containing 750 c.c. of 0·1*N*-NaOH. An anode consisting of a coil of platinum wire is placed in the porous cell, and the electrolysis carried out with a current of 2 amperes until the sodium hydroxide has increased in concentration by the calculated amount. When this state is reached, the anode solution is allowed to crystallize ; sodium paratungstate separates in large, vitreous crystals.

Several hydrates have been reported to have been obtained from the aq. soln. of sodium paratungstate. If the soln. be evaporated at ordinary or slightly elevated temp., the *octocosihydrate*, $5Na_2O.12WO_3.28H_2O$, or, according to C. Scheibler, $3Na_2O.7WO_3.16H_2O$, is formed. Analyses were reported by A. Laurent, J. C. G. de Marignac, E. Zettnow, O. W. Gibbs, G. von Knorre, C. Friedheim and R. Meyer, and L. A. Hallopeau. E. F. Anthon gave $Na_2O : WO_3 : H_2O = 1 : 2 : 4$; W. Lotz, 3 : 7 : 14 ; and V. Forcher, 2 : 5 : 12. The colourless or white crystals were found by J. C. G. de Marignac to be triclinic pinacoids with the axial ratios $a : b : c = 0·5341 : 1 : 1·1148$, and $\alpha = 93° 56'$; $\beta = 113° 36'$; and $\gamma = 85° 55'$. The habit is usually tabular. C. Scheibler thought that the crystals were monoclinic, and he gave 3·987 for the sp. gr. at 14°. According to E. F. Anthon, J. C. G. de Marignac, and C. Scheibler, the crystals are stable in air, but they effloresce in dried air ; thus, when kept over conc. sulphuric acid for 8 days two-thirds of the water was removed. At 100°, a loss of 10·42 to 12 per cent. was observed. A. Rosenheim found a loss of 24 mols. of water at 100°, and this led him to write the formula $Na_{10}H_4[H_4(WO_4)_6(W_2O_7)_3].24H_2O$, and later, $R_5H_5[H_2(WO_4)_6].nH_2O$; and A. Rosenheim and A. Wolff titrated the salt electrometrically with phenolphthalein as indicator and the results were in accord with this formula. H. Copaux observed a loss of 23 mols. of water at 110° ; 24 mols. at 150° ; 25·6 mols. at 200° ; and 26·6 mols. at 250°. E. F. Anthon, C. Scheibler, and J. C. G. de Marignac observed that almost the whole of the water is expelled at 300°, and the residue forms a clear soln. with water ; at a still higher temp., the salt melts forming a liquid which looks like a yellow oil. When the cold solid is extracted with water, there remains insoluble $Na_2O.4WO_3$, and Na_2WO_4 and $2Na_2O.3WO_3.7H_2O$ pass into soln. G. von Knorre said that the salt decomposes into Na_2WO_4 and $Na_2O.4WO_3$ when it is fused. F. Wöhler observed that when the dehydrated salt is heated in hydrogen, it forms a golden-yellow sodium-tungsten bronze; and L. A. Hallopeau observed that if heated with zinc powder, a golden-yellow sodium tungsten bronze is formed, as well as normal zinc tungstate, and, in some cases, tungsten itself. E. F. Anthon said that 100 parts of cold water dissolve 12·5 parts of salt. J. C. G. de Marignac said 8·33 parts, and V. Forcher, 7·94 parts at 22°. E. F. Anthon said that the aq. soln. tastes at first sweet, and then rough and bitter. J. C. G. de Marignac found that soln. of the salt saturated at 35° to 40°, and cooled to 18° to 20°, contain, per 100 parts of water, after standing for different periods of time:

	1	12	77	227	410 days
Salt .	10·81	8·88	9·16	8·40	8·52 parts

When heated, the solubility increases, and a deep-seated change occurs. Thus, a sat. soln. boiled for different periods of time, and cooled to 16° to 20°, contained in 100 parts of water:

	1	2	12	72	222	405 days
Salt .	147·0	109·8	38·6	14·5	10·26	11·36 parts

When these modified soln. are evaporated in air, the residue contains unchanged salt and $3Na_2O.7WO_3.21H_2O$. A. Rosenheim and A. Wolff gave for the solubility, *S* grms. per 100 grms. of soln.:

	0°	12°	21°	30°	40°	49°	59°	64°	73°
S . .	2·15	4·29	7·41	11·15	15·11	20·34	27·90	31·11	36·70

The vap. press. experiments over sulphuric acid of different sp. gr. indicated that there are 4 mols. of constitutional water. E. Wegelin measured the f.p. of soln. of sodium paratungstate, but was unable to decide between the 3 : 7-formula and the 5 : 12-formula. The calculated mol. wt. indicates that the salt in aq. soln. is probably resolved into sodium hydroxide and a metatungstate, and the results slightly favour the 3 : 7-formula. C. Scheibler said that the aq. soln. of sodium paratungstate has a neutral reaction; E. F. Anthon reported that it reddened blue litmus; G. von Knorre, that when freshly prepared, the aq. soln. is neutral, but when boiled and cooled, it is acid to phenolphthalien, and alkaline to tropæolin. It is assumed that when the soln. is kept for a long time, or boiled, it decomposes into normal sodium tungstate and $Na_2O.4WO_3.nH_2O$. H. Schmidt found that the salt can be titrated with a soln. of sodium hydroxide by using phenolphthalein or rosolic acid—*i.e.* aurin—as indicator; the results agreed with the 5 : 12-formula. G. Jander and co-workers' observations on the rate of diffusion, and the $H^{\cdot}$-ion concentration, agree with the assumption that the so-called sodium paratungstate is a hexatungstate. A. Rosenheim and A. Wolff found the eq. conductivity, λ mhos, for 0·1 mol $5Na_2O.12WO_3.nH_2O$ in v litres of water at 25°, to be:

v	32	64	128	256	512	1024
λ Made at 25° .	68·2	69·7	90·8	100·3	110	121·4
λ Boiled . .	89·4	96·6	106·3	116·3	126·6	136·3

J. Eltzbacher obtained much lower results; and A. Junius found that at 25° soln. with a mol of the salt in 25, 50, and 100 litres of water had the respective conductivities 61·2, 71·2, and 78·9 when prepared in the cold, and 82·4, 92·1 and 99·7 when prepared at 100°. R. G. Wells also noted that a change in the conductivity of soln. is produced by pre-heating, and this all agrees with the observations of J. C. G. de Marignac. For the observations of V. I. Spitzin and others on the reduction of sodium paratungstate, *vide supra*, tungsten bronzes. H. Uelsmann studied the action of hydrogen selenide on soln. of sodium paratungstate; and D. Klein, the action of polyhydric alcohols. J. C. G. de Marignac, F. Ullik, and

E. Zettnow observed that if a soln. of this salt be boiled for a long time with tungstic acid, an almost insoluble residue of variable composition is obtained.

With the *octocosihydrate*, $5Na_2O.12WO_3.28H_2O$, just described, C. Scheibler found that if a soln. be crystallized at 80° to 100°, or, according to J. C. G. de Marignac, at 60° to 80°, monoclinic prisms of the *pentacosihydrate*, $5Na_2O.12WO_3.25H_2O$, or $3Na_2O.7WO_3.14H_2O$ (C. Scheibler), with the axial ratios $a:b:c=0{\cdot}8069:1:0{\cdot}5328$, and $\beta=120°\ 10'$, are formed. J. C. G. de Marignac also reported that if the salt be crystallized from its aq. soln. at 100°, triclinic pinacoids of the *henicosihydrate*, $5Na_2O.12WO_3.21H_2O$, are formed. The crystals of octahedral habit have the axial ratios $a:b:c=0{\cdot}8695:1:1{\cdot}2787$, and $\alpha=91°\ 18'$, $\beta=86°\ 16'$, and $\gamma=97°\ 59'$. The salt loses nearly 15 mols. of water or 7·43 to 7·73 per cent. at 100°. While these two hydrates are referred by J. C. G. de Marignac to the 5 : 12-formula, there are two others which he referred to the 3 : 7-formula. If the aq. soln. of the 5 : 12 salt be mixed with some alkali carbonate, triclinic pinacoids of the *hexadecahydrate*, $3Na_2O.7WO_3.16H_2O$, are formed. The axial ratios are $a:b:c=0{\cdot}6836:1:1{\cdot}1802$, and $\alpha=95°\ 3'$, $\beta=123°\ 42'$, and $\gamma=91'\ 53'$. V. Forcher also reported a hydrate of the same composition from a soln. of tungstic acid and sodium carbonate. The salt loses 10·5 per cent. or 12 mols. of water at 100°. J. C. G. de Marignac obtained the *henicosihydrate*, $3Na_2O.7WO_3.21H_2O$, by boiling an aq. soln. of sodium paratungstate for a long time, and cooling—if necessary concentrating by evaporation. The triclinic pinacoids have the axial ratios $a:b:c=0{\cdot}9296:1:0{\cdot}5207$, and $\alpha=92°\ 47'$, $\beta=96°\ 28'$, and $\gamma=89°\ 40'$. This hydrate loses 14 per cent. or 17 mols. of water at 100°. When the hydrate is heated, it melts in its water of crystallization. It seems to dissolve in water more quickly than does the octocosihydrate of the 5 : 12-tungstate.

J. C. G. de Marignac allowed a soln. of ammonium paratungstate mixed with an excess of sodium paratungstate to crystallize, and obtained a crop of rhombic plates of **ammonium sodium 1 : 3-paratungstate,** $15(NH_4)_2O.5Na_2O.48WO_3.48H_2O$, followed by a mixture of this salt with the 3 : 2-paratungstate, and finally, the latter salt alone. The **ammonium sodium 3 : 2-paratungstate,** $3(NH_4)_2O.2Na_2O.12WO_3.15H_2O$, was also obtained by L. A. Hallopeau by adding ammonia, drop by drop, to a conc. soln. of sodium paratungstate, and concentrating the liquid for crystallization. J. C. G. de Marignac said that the crystals are rhombic bipyramids with the axial ratios $a:b:c=0{\cdot}9014:1:1{\cdot}4468$. L. A. Hallopeau added that 12 mols. of water are lost at 100°. W. Lotz found that if a soln. of a mol of normal sodium tungstate be poured into a boiling soln. of 4 mols of ammonium chloride, crystals of **ammonium sodium 4 : 1-paratungstate,** $4(NH_4)_2O.Na_2O.12WO_3.5H_2O$, are formed. The scaly crystals of the *pentahydrate* have a mother-of-pearl lustre ; A. Laurent represented it as a *heptahydrate ;* G. von Knorre represented it as a *tridecahydrate* ; and O. W. Gibbs reported a tetradecahydrate to be formed by adding a soln. of phosphoric acid neutralized by ammonia to an aq. soln. of normal sodium tungstate ; and L. A. Hallopeau, by adding an excess of ammonia to a conc. soln. of sodium paratungstate. The rhombic prisms lose 12 mols. of water at 100°. G. von Knorre reported the salt $2(NH_4)_2O.Na_2O.7WO_3.9H_2O$ to be formed in white scaly crystals from a soln. of a mol of sodium paratungstate and 2 mols of ammonium chloride, at 70°.

O. W. Gibbs reported **potassium paratungstate,** $5K_2O.12WO_3.10H_2O$, to be formed by boiling sodium decatungstate with potassium bromide or nitrate. The *decahydrate* forms a white, crystalline precipitate. He also said that a soln. of normal potassium tungstate is decomposed by boiling water with potassium hydroxide and paratungstate. E. Zettnow treated a soln. of sodium dodecatungstate with potassium nitrate and said that on crystallization the *tetradecahydrate,* $5K_2O.12WO_3.14H_2O$, or $3K_2O.7WO_3.8H_2O$, is formed. C. Scheibler, however, could obtain only the *henahydrate,* $5K_2O.12WO_3.11H_2O$, or $3K_2O.7WO_3.6H_2O$, by this process. A. Laurent's analysis agreed with that of

J. C. G. de Marignac. E. F. Anthon gave the formula $K_2O.2WO_3.2H_2O$, and A. Riche, $K_2O.2WO_3.3H_2O$. Analyses were also made by G. von Knorre, and E. Schaefer. E. F. Anthon prepared the henahydrate by boiling the dihydrate with a little water, filtering, and cooling; and also by adding tungstic acid to a boiling, aq. soln. of potassium hydroxide, carbonate, or normal tungstate so long as it dissolves, boiling the filtered soln., and cooling—C. Scheibler added that the mother-liquor contains metatungstate. A. Riche, and J. C. G. de Marignac prepared the salt by treating the normal tungstate with an acid, say by passing carbon dioxide through a filtered soln. obtained by melting wolframite with two-thirds its weight of potassium carbonate, and extracting the product with boiling water—C. Scheibler said that the extraction is best conducted by slowly adding the finely-powdered mass to boiling water. G. von Knorre said that this salt is obtained as a white precipitate by adding acetic acid to a conc. soln. of the normal tungstate—J. Lefort thought that the product is a ditungstate. E. Schaefer obtained it by electrolysis as indicated in connection with sodium paratungstate. J. C. G. de Marignac said that the thin six-sided plates are triclinic pinacoids with the axial ratios $a:b:c=0{\cdot}9137:1:1{\cdot}1362$, and $\alpha=65°\ 36'$, $\beta=117°\ 22'$, and $\gamma=115°\ 39'$; and they are isomorphous with the ammonium salt. The salt is stable in air; A. Riche said that the salt loses no water at 120°, and is dehydrated at 200°; and G. von Knorre said that only 1·44 per cent. of water is lost at 100°, and after heating for a long time at 200°, it retains one per cent. of water. H. Copaux observed that after heating to 110°, the salt retains 5·4 mols. of water; at 150°, 4·4 mols.; at 200°, 2·4 mols.; and at 250°, 1·4 mols. E. F. Anthon found that the dehydrated salt becomes yellow when heated, and melts below a red-heat to form a yellowish liquid which, when cooled, solidifies to a bluish or greenish, crystalline mass. G. von Knorre added that when the salt is fused, it forms the 5 : 14- and the normal tungstate. E. F. Anthon said that the salt is more easily soluble in hot than in cold water, and that the soln. reddens litmus, and has a rough and bitter taste. 100 parts of water at 16° dissolve one part of salt, and at 100°, 11·6 parts; on the other hand, J. C. G. de Marignac found that 100 parts of cold water dissolve 2·15 parts of salt, and with boiling water 6·6 parts of salt. If the crystalline powder be shaken for many days with water at 20°, 100 parts of water dissolve 1·4 parts of salt; if the salt be boiled many days with water, 100 parts of water at 18° contain 17·8 parts of salt, and on evaporating the liquid in dry air, it furnishes a white, amorphous mass. If the salt be kept in a closed vessel for many days, it seems to decompose forming a more soluble variety since after keeping for 1, 26, 153, and 334 days, the respective solubilities per 100 parts of water are 17·8, 8·4, 6·4 and 6·4. A. Rosenheim and A. Wolff found that when the sodium salt is boiled with arsenious oxide, and the soln. treated with potassium chloride, **potassium arsenitotungstate** is formed, $7K_2O.As_2O_3.18WO_3.24H_2O$; and similarly, with antimonious oxide, **potassium antimonitotungstate,** $8K_2O.Sb_2O_3.19WO_3.37H_2O$, was formed; and similarly with salts of other bases—ammonium, guanidine, barium, etc.

E. Schaefer fused an equimolar mixture of rubidium carbonate and tungsten trioxide, extracted the cold product with water, and boiled the liquid with enough hydrochloric acid to prevent blue litmus becoming red. On cooling, the liquid deposits white, **rubidium paratungstate,** $5Rb_2O.12WO_3.18H_2O$. When strongly heated, the salt melts and some rubidium is lost by volatilization. The salt is less soluble in water. The powdered salt is decomposed by evaporation with aqua regia a number of times.

C. Gonzalez prepared **copper paratungstate,** $5CuO.12WO_3.33H_2O$, or $3CuO.7WO_3.19H_2O$, from soln. of sodium paratungstate and copper sulphate; and G. von Knorre recommended using an excess of copper sulphate—say one mol of tungstate and 3 mols of the copper salt—at 70°. The bluish-green, microcrystalline precipitate does not melt at a red-heat, but after the ignition it is lemon-yellow. The salt is insoluble in water, but dissolves in water containing a few drops of nitric acid, and the clear soln. gelatinizes after standing for some time. If equimolar proportions of the tungstate and copper salt be mixed in soln., at 70°, G. von Knorre found that **sodium copper paratungstate,** $3Na_2O.3CuO.14WO_3.32H_2O$, is formed, as a green crystalline precipitate; and C. Gonzalez obtained pale blue needles of $4Na_2O.CuO.12WO_3.32H_2O$, by adding a soln. of copper sulphate to a boiling soln. of sodium paratungstate so long as the precipitate redissolves. The slightly turbid liquid is filtered rapidly, washed with cold water, and dried in air. It melts at a red-heat. According to S. Traverso, **cupro-scheelite** can be regarded as a **calcium copper tungstate,** and a variety from Villa Salto, Sardinia, corresponds with $2CaWO_4.CuWO_4$. I. Domeyko also found a variety at Llamuco, Chili; and J. D. Whitney, at La Paz, California. C. Gonzalez prepared **silver paratungstate,** $5Ag_2O.12WO_3.28H_2O$, by adding a soln. of silver nitrate to one of sodium paratungstate. The white, crystalline *octocosihydrate* becomes grey when dried at 60°, and is then an *octohydrate*. The salt melts at a red-heat, and solidifies on cooling to a mass of tabular crystals.

According to G. von Knorre, if a soln. of sodium paratungstate be treated with an excess of calcium chloride, a voluminous, white precipitate is formed, which, when digested with the mother-liquor, becomes granular and crystalline; when washed and dried, it is **calcium paratungstate,** $3CaO.7WO_3.18H_2O$. It does not melt at a red-heat; and at 100°, it loses 8·03 per cent. of water. It is more soluble than the strontium and barium salts. According to C. Gonzalez, if the aq. soln. of calcium chloride be added until the precipitate first formed no longer dissolves, and the slightly turbid soln. be rapidly filtered, white crystals of **sodium calcium paratungstate,** $3Na_2O.2CaO.12WO_3.34H_2O$, are formed. G. von Knorre prepared **strontium paratungstate,** $3SrO.7WO_3.16H_2O$, by the method used for the calcium salt. A. Rosenheim and A. Wolff gave for the strontium salt $5SrO.12WO_3.28H_2O$. W. Lotz also obtained it by mixing soln. of ammonium paratungstate and strontium chloride. It does not fuse at a red-heat; at 100°, it loses 8·53 per cent. of water, and 13·27 per cent. at a red-heat. C. Gonzalez prepared **sodium strontium paratungstate,** $Na_2O.4SrO.12WO_3.29H_2O$, as in the case of the calcium strontium salt. The white, scaly crystals do not melt at a red-heat. G. von Knorre prepared **barium paratungstate,** $3BaO.7WO_3.16H_2O$, by the method employed for the calcium salt. A. Rosenheim and A. Wolff gave for the barium salt $5BaO.12WO_3.28H_2O$. It loses 8·8 per cent. of water at 100°, and when dried over sulphuric acid, 8 mols. It is insoluble in cold water, and slightly soluble in hot water. W. Lotz obtained the *octohydrate* from soln. of barium chloride, and ammonium paratungstate. It loses 3·29 per cent. of water at 100°. This salt was also prepared by L. A. Hallopeau. C. Scheibler found that microscopic plates of **sodium barium paratungstate,** $3Na_2O.2BaO.12WO_3.24H_2O$, or $2Na_2O.BaO.7WO_3.14H_2O$, separate when an excess of baryta-water is added to a boiling soln. of sodium paratungstate, and the liquid cooled. This salt was also prepared by L. A. Hallopeau.

G. von Knorre prepared **magnesium paratungstate,** $3MgO.7WO_3.24H_2O$, by adding a soln. of a mol of sodium paratungstate to a soln. of an excess (3 mols) of magnesium sulphate. The white, crystalline powder is sparingly soluble in cold water, and more soluble in hot water; it is decomposed by acids. W. Lotz, and J. C. G. de Marignac prepared **ammonium magnesium paratungstate,** $2(NH_4)_2O.3MgO.12WO_3.24H_2O$, by mixing hot, conc. soln. of magnesium sulphate and ammonium paratungstate. No precipitation occurs with cold soln. The small, rhombic crystals are sparingly soluble in water. G. von Knorre obtained a white crystalline mass of **sodium magnesium paratungstate,** $3Na_2O.3MgO.14WO_3.33H_2O$, by mixing soln. of 20 grms. of hydrated sodium paratungstate in 15 c.c. of water at 70°, and 2·3 grms. of hydrated magnesium sulphate in 10 c.c. of water. L. A. Hallopeau also obtained **potassium magnesium paratungstate,** $5(\frac{2}{3}K_2O.\frac{1}{3}MgO).12WO_3.24H_2O$, by mixing equimolar proportions of soln. of potassium paratungstate, and magnesium sulphate, and concentrating the soln. The salt, recrystallized from hot water, forms microscopic prisms, almost insoluble in cold water. The crystals lose 17 mols. of water at 100°. C. Gonzalez obtained white needles of **zinc paratungstate,** $5ZnO.12WO_3.37H_2O$, by treating an excess of a soln. of a zinc salt with one of sodium paratungstate. A. Rosenheim and A. Wolff gave $5ZnO.12WO_3.35H_2O$. The salt dissolves in water acidified with a few drops of nitric acid, but the clear soln. soon gelatinizes. W. Lotz prepared **ammonium zinc paratungstate,** $(NH_4)_2O.2ZnO.7WO_3.13H_2O$, in snow-white needles, by adding ammonium paratungstate to a soln. of zinc sulphate. The salt is soluble in boiling water, and more soluble in water containing ammonium tungstate, or oxalic, tartaric, or phosphoric acid. The salt loses 8 mols. of water at 100°. G. von Knorre found that a boiling soln. of a mol of sodium paratungstate and 2 mols of zinc sulphate deposits white needles of **sodium zinc paratungstate,** $Na_2O.2ZnO.7WO_3.15H_2O$, on cooling. The salt is sparingly soluble in cold water; and is decomposed by mineral acids. L. A. Hallopeau obtained a **potassium zinc paratungstate** by precipitation from potassium paratungstate by means of zinc sulphate. C. Gonzalez prepared **cadmium paratungstate,** $5CdO.12WO_3.16H_2O$, as a white crystalline precipitate by the method employed for the zinc salt. W. Lotz treated cadmium sulphate with ammonium paratungstate and obtained white needles of **ammonium cadmium paratungstate,** $3(NH_4)_2O.12CdO.35WO_3.35H_2O$. The voluminous precipitate becomes grey when heated, then orange-yellow, and on cooling pale yellow. 12 mols. of water are expelled at 100°. G. von Knorre prepared the **sodium cadmium paratungstate,** $Na_2O.2CdO.7WO_3$, as in the case of the corresponding zinc salt. For **mercurous paratungstate,** *vide infra,* mercurous metatungstate.

W. Lotz reported **aluminium paratungstate,** $Al_2O_3.7WO_3.9H_2O$, to be formed as a white, caseous precipitate, by mixing soln. of ammonium paratungstate and an aluminium salt. The precipitate dissolves in an aq. soln. of alum. E. Schaefer added an excess of a soln. of thallous sulphate to one of sodium paratungstate and obtained a white precipitate of **thallous paratungstate,** $5Tl_2O.12WO_3.9H_2O$; it loses its water when dried in a desiccator, and melts at a red-heat with the volatilization of some thallium. It is insoluble in water but soluble in soln. of alkali carbonate or hydroxide, and it is decomposed by mineral acids. C. Gonzalez could not prepare thallous paratungstate. For **cerous, lanthanum, didymium, gadolinium, yttrium, and ytterbium paratungstates,** *vide supra,* the rare earth tungstates.

W. Lotz, and J. J. Berzelius obtained **lead paratungstate,** $3PbO.7WO_3.10H_2O$, by treating a soln. of a lead salt with one of ammonium paratungstate, washing the precipitate by decantation; and drying it in air. The white, powdered *decahydrate* forms the trihydrate when dried at 100°, and it becomes sulphur-yellow, and anhydrous after heating to redness. The hydrate is insoluble in water, and in soln. of ammonium paratungstate and of lead nitrate, but it is soluble in soda-lye, and boiling phosphoric acid. C. Gonzalez obtained white needles of **sodium lead paratungstate,** $4Na_2O.PbO.12WO_3.29H_2O$, by adding a soln. of a lead salt to a boiling soln. of sodium paratungstate until the precipitate no longer redissolves; the faintly turbid soln. is filtered and allowed to stand for a few hours. The salt melts at a red-heat.

W. Lotz reported **chromium paratungstate,** $Cr_2O_3.7WO_3.nH_2O$, by mixing soln. of sodium paratungstate and chromic chloride. The pale greyish-green powder after calcination appears straw-yellow with a tinge of green. When dried at 100° after calcination it loses 9 mols. or 8·06 per cent. of water. The compound is insoluble in water or a soln. of acid ammonium tungstate, but soluble in a soln. of chromic chloride. W. Lotz, and E. F. Anthon found that **manganese paratungstate,** $5MnO.12WO_3.18H_2O$, or $3MnO.7WO_3.11H_2O$, is precipitated by adding sodium paratungstate to a manganous salt. The white powder has a yellow tinge, and when heated to redness, it loses its water, and becomes yellow. When the octodecahydrate is dried over conc. sulphuric acid, it loses 2·79 per cent. or about 5 mols. of water. E. F. Anthon represented the salt by the formula $MnO.2WO_3.3H_2O$, and he said that it is soluble in phosphoric, nitric, or oxalic acid. When the soln. in nitric acid is boiled, yellow tungstic acid separates out. C. Gonzalez said that the precipitate is the *tetratriacontahydrate,* $3MnO.7WO_3.20H_2O$, or $5MnO.12WO_3.34H_2O$. G. von Knorre prepared white or pale yellow crystals of **sodium manganous paratungstate,** $3Na_2O.3MnO.14WO_3.36H_2O$, by mixing soln. of equimolar proportions of manganous sulphate and sodium paratungstate at 70°. Part of the salt separates out at once, and part separates gradually as the soln. cools. L. A. Hallopeau obtained **potassium manganous paratungstate,** $3K_2O.2MnO.12WO_3.16H_2O$, by mixing equimolar soln. of manganous sulphate, and potassium paratungstate. The white precipitate has a tinge of yellow, and it consists of microscopic, rhombic prisms, which lose about 10 mols. of water at 100°. The salt is insoluble in water. A. Rogers and E. F. Smith's **ammonium manganic paratungstate** is described in connection with the normal tungstates.

E. F. Anthon observed that a soln. of ammonium paratungstate precipitates yellow **ferrous paratungstate** from a soln. of ferrous chloride. C. Gonzalez prepared **cobaltous paratungstate,** $3CoO.7WO_3.25H_2O$, by adding a boiling soln. of sodium paratungstate to one of cobalt sulphate. If the admixing is reversed, some double salt may be formed. The oily, viscid mass forms, on cooling, a pale rose-coloured, microcrystalline powder ; it does not melt at a red-heat, and when the ignited salt is cooled, it is blue. As just indicated, if cobalt sulphate be added to sodium paratungstate, in boiling soln., **sodium cobaltous paratungstate,** $3Na_2O.2CoO.12WO_3.30H_2O$, separates out if the filtered soln. is allowed to stand for a few hours. The rose-red crystals become bluish-green after ignition, and they melt at a red-heat. E. F. Anthon, and W. Lotz prepared **nickelous paratungstate,** $3NiO.7WO_3.14H_2O$, by adding a soln. of alkali paratungstate to one of a nickel salt ; the pale green precipitate dries to a pale green powder. E. F. Anthon represented it by the formula $NiO.2WO_3.4H_2O$, but W. Lotz showed that it is a paratungstate. When heated to redness, the salt becomes brown, and sinters. The original salt is insoluble in water, sparingly soluble in oxalic acid, and soluble in warm phosphoric acid, and in acetic acid. A. Wolff, and A. Rosenheim and A. Wolff described an **ammonium ferric paratungstate,** $3(NH_4)_2O.Fe_2O_3.12WO_3.27H_2O$, as well as **guanidinium ferric paratungstate,** $2{\cdot}5(CN_3H_6)_2O.Fe_2O_3.12WO_3.17H_2O$.

REFERENCES.

[1] A. Rosenheim, *Zeit. anorg. Chem.*, **96**. 139, 1916 ; G. Jander, D. Mojert and T. Aden, *ib.*, **180**. 129, 1929 ; C. Friedheim and R. Meyer, *ib.*, **1**. 76, 1892 ; J. Lefort, *Compt. Rend.*, **82**. 1182, 1876 ; *Ann. Chim. Phys.*, (5), **9**. 93, 1876 ; J. C. G. de Marignac, *ib.*, (3), **69**. 5, 1863 ; (4), **3**. 76, 1864 ; *Compt. Rend.*, **55**. 888, 1862 ; **58**. 809, 1864 ; A. Laurent, *ib.*, **25**. 538, 1847 ; *Ann. Chim. Phys.*, (3), **21**. 59, 1847 ; L. A. Hallopeau, *ib.*, (7), **19**. 96, 1900 ; *Compt. Rend.*, **139**. 283. 1904 ; F. J. Malaguti, *Ann. Chim. Phys.*, (2), **60**. 271, 1835 ; A. Riche, *ib.*, (3), **50**. 67, 1857 ; D. Klein, *ib.*, (5), **28**. 427, 1883 ; *Compt. Rend.*, **86**. 826, 1876 ; **99**. 144, 1884 ; H. Copaux, *ib.*, **156**. 1771, 1913 ; T. M. Taylor, *Journ. Amer. Chem. Soc.*, **24**. 629, 1902 ; E. F. Smith, *Chem. News*, **129**. 198, 207, 224, 240, 257, 286, 1924 ; *Journ. Amer. Chem. Soc.*, **44**. 2027, 1922 ; R. G. Wells, *ib.*, **29**. 112, 1907 ; W. Lotz, *Liebig's Ann.*, **91**. 45, 1854 ; *Journ. prakt. Chem.*, (1), **63**, 209, 1854 ; *Ann. Chim. Phys.*, (3), **43**. 246, 1855 ; J. J. Berzelius, *Schweigger's Journ.*, **16**. 476, 1816 ; *Ann. Phil.*, **3**. 245, 1814 ; *Ann. Chim. Phys.*, (2), **17**. 13, 1821 ; *Pogg. Ann.*, **4**. 147, 1825 ; **8**. 147, 267, 1826 ; J. J. and F. de Elhuyar, *Análisis quimico del volfram y examén de un nuovo metal que entra en su composicion*, Bascongada, 1783 ; *A Chemical Examination of Wolfram and Examination of a New Metal which enters into its Composition*, London, 1785 ; *Chemische Zerkleiderung des Wolframs*, Halle, 1786 ; *Mém. Acad. Toulouse*, **2**. 141, 1784 ; K. H. T. Kerndt, *Phil. Mag.*, (3), **31**. 253, 1847 ; *Journ. prakt. Chem.*, (1), **41**. 190, 1847 ; (1), **42**. 81, 1847 ; E. F. Anthon, *ib.*, (1), **8**. 404, 1836 ; (1), **9**. 341, 1836 ; C. Gonzalez, *ib.*, (2), **36**. 44, 1887 ; G. von Knorre, *Ber.*, **18**. 2362, 1885 ; **19**. 819, 1886 ; *Journ. prakt. Chem.*, (2), **27**. 49, 1883 ; C. Scheibler, *ib.*, (1), **80**. 204, 1860 ; (1), **83**. 273, 1861 ; *Chem. News*, **6**. 181, 1862 ; *Sitzber. Akad. Berlin*, 208, 1860 ; O. W. Gibbs, *Proc. Amer. Acad.*, **15**. 1, 1879 ; **21**. 77, 1885 ; *Amer. Chem. Journ.*, **1**. 2, 217, 1880 ; H. Schmidt, *ib.*, **8**. 16, 1886 ; B. Kellner, *Untersuchungen über Perwolframate*, Berlin, 1909 ; J. Schabus, *Bestimmung der Krystallgestalten in chemischen Laboratorien erzeugter Produkte*, Wien, 38, 1855 ; E. Zettnow, *Pogg. Ann.*, **130**. 248, 1867 ; A. Pinagel, *Beiträge zur Kenntnis der*

Wolframate und Silicowolframate, Bern, 1904; A. Lottermoser, *Zeit. Koll.*, **30**. 346, 1922; V. Forcher, *Sitzber. Akad. Wien*, **44**. 164, 1862; *Journ. prakt. Chem.*, (1), **86**. 227, 1862; *Bull. Soc. Chim.*, (2), **5**. 197, 1863; J. Eltzbacher, *Beiträge zur Elektrochemie der Wolframate*, Berlin, 1899; A. Junius, *Beiträge zur Kenntnis der Molybdate*, Berlin, 1905; F. Wöhler, *Pogg. Ann.*, **2**. 345, 1824; H. Uelsmann, *Liebig's Ann.*, **116**. 122, 1860; E. Wegelin, *Zur Kenntnis einiger Natriumwolframate*, Zürich, 1906; S. Traverso, *Resocconti Riunioni Soc. Min. Sarda*, (8), **6**. 8, 1903; J. D. Whitney, *Proc. Cal. Acad.*, **3**. 287, 1866; I. Domeyko, *Ann. Mines*, (4), **3**. 15, 1843; E. Schaefer, *Beiträge zur Kenntnis der Wolframverbindungen*, Berlin, 1903; *Zeit. anorg. Chem.*, **38**. 143, 1904; V. I. Spitzin, *Zeit. anorg. Chem.*, **148**. 69, 1925; *Journ. Russ. Phys. Chem. Soc.*, **58**. 474, 1926; E. F. Smith, *Proc. Amer. Phil. Soc.*, **65**. 10, 18, 1926; A. Rogers and E. F. Smith, *Journ. Amer. Chem. Soc.*, **26**. 1474, 1904; A. Wolff, *Zur Kenntnis der Parawolframate und einiger Heteropolywolframate*, Berlin, 1930; A. Rosenheim and A. Wolff, *Zeit. anorg. Chem.*, **193**. 47, 64, 1930; F. Ullik, *Sitzber. Akad. Wien*, **56**. 157, 1867.

§ 15. The Metatungstates, and Tetratungstates

F. Margueritte[1] boiled hydrated tungsten trioxide with an aq. soln. of ammonium tungstate or ammonia; some tungsten trioxide may separate from the soln. on cooling and evaporation, but afterwards the so-called **ammonium metatungstate,** $(NH_4)_2O.4WO_3.8H_2O$, is formed. A. Laurent as well as A. Riche, and V. Forcher boiled a soln. of ordinary or less acid ammonium tungstates for many hours, and obtained this salt by cooling the liquor. W. Lotz added that the conversion to metatungstate is incomplete after the soln. has been boiled for many days. T. M. Taylor boiled a soln. of the paratungstate for 2 or 3 days, and obtained the salt by evaporation—*vide infra*, the hexatungstate. A. Laurent treated an aq. soln. of ammonium tungstate with dil. nitric acid, and evaporated the filtered soln.; W. Lotz added that it is difficult to free the product from ammonium nitrate. C. Scheibler heated between 250° to 300° a thin layer of crystalline ammonium tungstate in a porcelain dish so long as ammonia is given off; and an aq. soln. of the residue after filtration furnishes crystals of this salt. T. M. Taylor heated ammonium paratungstate for 4 hrs. at 150° and obtained the metatungstate. E. F. Smith recommended saturating a hot soln. of purified ammonium paratungstate with a warm emulsion of tungstic acid; and concentrating the filtrate either at 70°, or spontaneously at ordinary temp. Methods of preparation were also described by J. Persoz, G. N. Wyrouboff, and J. C. G. de Marignac. Analyses were made by J. C. G. de Marignac, A. Laurent, W. Lotz, A. Riche, C. Scheibler, J. Persoz, F. Margueritte, and H. Copaux. F. Margueritte represented his results by $(NH_4)_2O.3WO_3.5H_2O$; A. Laurent, by $5(NH_4)_2O.H_2O.18WO_3.30H_2O$; W. Lotz, by $2(NH_4)_2O.8WO_3.5H_2O$; and C. Scheibler, by $(NH_4)_2O.4WO_3.8H_2O$. The best representative formula is based on the hypothesis that the parent acid is $H_{10}[H_2(W_2O_7)_6]$, and the octohydrated ammonium salt is symbolized $(NH_4)_6H_4[H_2(W_2O_7)_6].5H_2O$. If this hypothesis be correct, then the anhydrous salts $R_2O.4WO_3$ are not metatungstates at all, and can be provisionally regarded as tetratungstates. J. C. G. de Marignac found that when alcohol is added to a hot aq. soln. of ammonium metatungstate, monoclinic prisms of the *hexahydrate* are formed; the axial ratios are $a:b:c=0·8121:1:0·7963$, and $\beta=95° 9'$; the salt loses nearly 5 mols. of water at 100°; and the aq. soln. has a neutral reaction. A. Riche reported a *tetrahydrate*, but J. C. G. de Marignac showed that the product was probably a silicotungstate.

F. Margueritte, A. Laurent, C. Scheibler, and A. Riche described the colourless crystals of ammonium metatungstate as regular octahedra; W. Lotz, as tetragonal crystals, which, according to G. N. Wyrouboff, have the axial ratio $a:c=1:0·9747$. H. Copaux gave 1 : 1·012 for the axial ratio, and added that they are isomorphous with $5(NH_4)_2O.B_2O_3.24WO_3.52H_2O$. G. N. Wyrouboff found that the crystals are isomorphous with those of the metatungstates of sodium, cadmium, and manganese. The birefringence is strong and positive. C. Scheibler found that the crystals effloresce rapidly in air; F. Margueritte, and A. Riche, that they melt in their water of crystallization; and T. M. Taylor, that they begin to give off ammonia at 120°. The salt loses about 7 mols. of water at 100°, but the remaining mol. cannot be expelled below 200°. The residue remaining after the expulsion of water at 100°, namely, $(NH_4)_2O.4WO_3.H_2O$, or $2NH_4OH.4WO_3$, is the most stable form of the ammonium tungstates, and T. M. Taylor represented the ammonium tungstates as salts containing this as a nucleus. W. Lotz said that 12·17 per cent. of water is lost at 100°; G. N. Wyrouboff, 7 mols. at 105°; J. C. G. de Marignac, 10·84 per cent. or about 7 mols.; A. Laurent, 11 per cent. at 200°; and A. Riche, 10·95 per cent. at 100° or in vacuo. The salt is freely soluble in water—thus A. Riche found that 100 parts of water at ordinary temp. dissolve nearly 300 parts of the salt; and W. Lotz, 117·6 parts at 15°. The solubility increases rapidly with a rise of temp., and W. Lotz found that the soln. sat. at 40° is almost solid at ordinary temp. C. Scheibler said that the aq. soln. has a high index of refraction; and J. C. G. de Marignac, that it is almost neutral; conc. hydrochloric acid precipitates ammonium chloride and the 3 : 16-tungstate. V. I. Spitzin and L. Kaschtanoff found that with hydrogen chloride, tungsten dioxydichloride and sodium ditungstate are formed, and the latter then reacts as previously indicated. A. Riche found that hydrogen sulphide forms a soluble sulpho-salt; and W. Lotz, that ammonia transforms the salt in soln. into ordinary ammonium tungstate. T. M. Taylor found that when ammonia is passed over ammonium metatungstate at ordinary temp., needle-like crystals of ammonium tungstate are formed; and at 100°, plates of the paratungstate are formed. W. Lotz said that ordinary alcohol dissolves a little metatungstate, but absolute alcohol dissolves none; and J. C. G. de Marignac added that alcohol precipitates the metatungstate from its hot, aq. soln. A. Riche found that the salt is insoluble in ether. W. Lotz observed that with potassium ferrocyanide and hydrochloric acid, no precipitation occurs; and in opposition to a statement of F. Margueritte, alkali hydroxides or carbonates give no precipitate when added to the aq. soln. of the salt; silver nitrate gives a precipitate when ammonia is also added, and the precipitate is soluble in hot water. When ammonium or sodium metatungstate is gently heated with sodium chromate, E. F. Smith found that the filtered soln., on standing, deposits crystals of $4Na_2O.10WO_3.23H_2O$, and sodium molybdate also gives the corresponding salt. No tungsten trioxide is formed by heating the product to 250° in dry hydrogen chloride. No complex $m Na_2MoO_4.n Na_2W_4O_{13}$ was formed.

C. Scheibler obtained **lithium metatungstate,** $Li_2O.4WO_3.nH_2O$, by the action of a soln. of lithium carbonate on an excess of hydrated tungsten trioxide, and by the action of lithium sulphate on a soln. of the barium salt. The evaporation of the aq. soln. furnishes a non-crystallizable syrup. F. Hoermann, Fig. 25, found that the salt has an incongruent m.p. at 800°. G. von Knorre fused together a mixture of 5 mols of lithium carbonate and 12 mols of tungsten trioxide, and extracted the mass with boiling water. There remained needle-like prisms of **sodium tetratungstate,** $Li_2W_4O_{13}$—*vide supra*, O. Brunner on the tungsten bronzes. C. Scheibler obtained **sodium tetratungstate,** $Na_2O.4WO_3$, by heating the coarsely powdered paratungstate to redness, and extracting the mass with hot water; there remained thin scales of this salt. At a much higher temp., the paratungstate partly sinters, and forms bluish-green plates or cubes. F. Hoermann, Fig. 25, found that the salt has an incongruent m.p. at 784°. G. von Knorre said that if the metatungstate be melted, and afterwards extracted with water, there remains the octotungstate. C. Friedheim said that if the salt be dried at 110° to 120°, and then treated with water, normal sodium tungstate passes into soln. C. Scheibler, J. Eltzbacher, and H. Copaux prepared **sodium metatungstate,** $Na_2O.4WO_3.10H_2O$, by boiling an aq. soln. of the paratungstate with an excess of hydrated tungsten trioxide until the filtered soln. no longer gave a precipitate with hydrochloric acid. According to E. Wegelin, a reversible reaction is involved: $3Na_2W_4O_{13}.Aq.+5H_2O \rightleftharpoons 5H_2WO_4+3Na_2O.7WO.Aq.$ The aq. soln. was then concentrated over a water-bath, and allowed to crystallize over conc. sulphuric acid. C. Scheibler also prepared the metatungstate by treating a sat. aq. soln. of normal sodium tungstate with a large excess of conc. acetic acid. A heavy, oily layer of a conc. soln. of the metatungstate settles at the bottom of the vessel. F. Margueritte added a mineral acid to a conc. soln. of the paratungstate until the precipitate no longer redissolved. V. Forcher observed that this mode of preparation is not so good as that of C. Scheibler. E. F. Smith recommended the following process :

> First purify ordinary sodium paratungstate by about a dozen recrystallizations from aq. soln. Heat the aq. soln. at 70° to 75°, and add an emulsion of tungstic acid at 65° to 70°. When the soln. on agitation dissolves no more tungstic acid, it is allowed to stand overnight and filtered. The colourless, clear liquid is then evaporated at a temp. not exceeding 70°, and, when sufficiently concentrated, allowed to remain in the cold. Colourless crystals are formed, which, on placing between the finger and thumb, exhibit none of the stickiness which occurs when impure sodium paratungstate has been used. A soln. of the salt, recrystallized from water, should give no permanent precipitate when treated with a slightly acidulated soln. of barium chloride.

A. Lottermoser prepared the alkali metatungstates by the electrolysis of an aq. soln. of the normal tungstate in a partitioned cell until the anode liquor contained sufficient tungstic acid to form the metatungstate. The salt was analyzed by C. Scheibler, and V. Forcher ; R. C. Wells' analysis of a sample gave $3Na_2O.8WO_3.17H_2O$. E. F. Smith found that the composition of the dehydration product agrees with the formula $5(Na_2O.WO_3).7(H_2O.WO_3).21H_2O$. The colourless, octahedral crystals were considered by C. Scheibler to belong to the cubic system ; but C. F. Rammelsberg showed that they are tetragonal bipyramids with the axial ratio $a:c=1:0{\cdot}9930$, and G. N. Wyrouboff added that the salt is isomorphous with the tungstates of ammonium, cadmium, and manganese. The birefringence is fairly strong and positive. A slight reduction of the tungstate, said V. Forcher, may impart a bluish tinge. C. Scheibler gave 3·847 for the sp. gr. at 13° ; M. Soboleff gave 4·04. V. Forcher found the crystals are stable in air, but they effloresce in dry air ; they lose the greater part of their water over sulphuric acid ; when heated, the salt appears yellow, and on cooling, bluish-grey. If the ignited salt be extracted with water, normal sodium tungstate passes into soln. According to C. Friedheim, 7 mols. of water are expelled at 120°, and the remainder at a higher temp.—one mol. of water is still present at 240°. A. P. Sabanéeff made some observations on this subject. E. F. Smith found that the dehydrated salt melts at 706·6°. E. Wegelin found that the effect of the salt on the f.p. of water agrees with the assumption that the mol. wt. is 497 to 502—the theoretical value $Na_2W_4O_{13}$ is 990, so that on this hypothesis the salt furnishes two ions. A. P. Sabanéeff also made determinations of the f.p. of aq. soln. of the salt ; and G. Tammann found that the vap. press. of soln. of 24·01, 89·90, and 332·8 grms. of $Na_2W_4O_{13}$ in 100 grms. of water are respectively 6·4, 19·0, and 132·2 mm. lower than the value for water alone. M. Soboleff found the eq. electrical conductivity of soln. of an eq. of the salt in v litres of water, at 25°, to be :

v . .	32	64	128	256	512	1024
λ . .	89·3	98·7	107·6	116·6	126·0	134·1 mhos.

J. Eltzbacher's values are probably too low. A. Rosenheim and F. Kohn found $\lambda_{1024}-\lambda_{32}=38{\cdot}4$. E. Wegelin found that on electrolysis of aq. soln., the hydrogen and oxygen are given off in the proportions 2 : 1 in agreement with the assumption that no pertungstate is formed. The salt is extremely soluble in water. V. Forcher found that 100 parts of water at 19° dissolve 512 parts of salt ; and C. Scheibler, that 100 parts of water at 13° dissolve 1069 parts of salt, and the sp. gr. of the soln. is 3·02. The aq. soln. has a bitter taste, and it shows the ordinary reactions of the metatungstate. It gives precipitates with salts of the metals. F. Margueritte said that acidic soln. of the salt yield plates of the *trihydrate*, but this has not been confirmed. According to C. Schön, if cotton be worked in a 5 per cent. soln. of sodium metatungstate, it rapidly becomes blue when exposed to light, owing to the reduction of the compound. In a dark room the fabric again becomes white, the blue colour reappearing on renewed exposure to light. On treating the blue fabric with water a blue soln. is obtained, which, on the addition of lead acetate, gives a blue precipitate. Both the soln. and precipitate rapidly become colourless, even in full daylight. A simple soln. of the metatungstate does not change colour. The effect of adding a salt of copper to the metatungstate is to retard though not to prevent the action of light; fabrics prepared with metatungstate and a copper salt become at first yellower and then slowly bluer. The reducing action of light is partly overcome by the oxidizing properties of the copper salts. The observations of T. Graham, W. Biltz and A. von Vegesack, A. P. Sabanéeff, and N. Pappada on colloidal soln. of the salt have been discussed in connection with colloidal tungstic acid (*q.v.*). A. Rosenheim and F. Kohn treated 5 c.c. of $\frac{1}{10}N$-$H_2W_4O_{13}$ with increasing sp. conductivity at 25°. The results are summarized in Fig. 50. The results show that there is a definite break with the addition of 2 mols. of NaOH to a mol. of $H_2W_4O_{13}$ corresponding with the formation of $Na_2O.4WO_3$; and also a feeble change of curvature corresponding with the conversion of the metatungstate into normal tungstate. For the observations of V. I. Spitzin and others on the reduction of the tetratungstates, *vide supra*, tungsten bronzes. W. I. Baragiola obtained octahedral crystals of what is probably an isomorphous mixture, **ammonium sodium 1 : 3-metatungstate,** $(NH_4)_2O.3Na_2O.16WO_3.38H_2O$, from a soln. of ammonium and sodium metatungstates—the latter in excess. J. Lefort studied the action of quinine on the alkali metatungstates. The methods of preparing aq. soln. of **potassium metatungstate,** $K_2O.4WO_3.nH_2O$, are similar to those employed for the sodium salt. Several hydrates have been reported. C. Scheibler obtained the *octohydrate*, $K_2O.4WO_3.8H_2O$, by crystallization from an aq. soln. of the salt, according to H. Copaux, at a low temp.; or, according to C. Scheibler, from the mother-liquor obtained in preparing the paratungstate. G. N. Wyrouboff said that the octahedral crystals belong to the tetragonal system. They quickly effloresce in air, and lose 7 mols. of water at 100°. Along with the octahedral crystals, C. Scheibler, and J. C. G. de Marignac observed some acicular crystals which may be one of the lower hydrates. J. C. G. de Marignac prepared the *pentahydrate*, $K_2O.4WO_3.5H_2O$, by treating an aq. soln. of the salt with alcohol. The precipitate dissolves when the soln. is warmed, and on cooling, monoclinic prisms are deposited. They have the axial ratios $a : b : c = 0{\cdot}5945 : 1 : 0{\cdot}6609$, and $\beta = 123°\ 0'$. The birefringence is strong and positive. The hydrate does not effloresce in the cold, but at 100°, it loses 4 mols. of water. The hydrate is freely soluble in water. H. Copaux reported the hemitridecahydrate, $K_2O.4WO_3.6\frac{1}{2}H_2O$, or $6K_2O(3H_2O).24WO_3.36H_2O$, to be deposited from a soln. at 30°. The doubly refracting, hexagonal prisms have the axial ratio $a : c = 1 : 0{\cdot}659$, and they are isomorphous with potassium borotungstate or silicotungstate. The crystals are optically active in having a dextrorotary power for the *D*-line of 9°. H. Copaux also obtained the *octohydrate* from an aq. soln. of this salt at a low temp. Crystals of what were probably potassium metatungstate were also reported by F. Margueritte, A. Riche, and J. Lefort. F. Hoermann found that the tetratungstate has an incongruent m.p. at 930°—Fig. 35. G. N. Wyrouboff reported **rubidium metatungstate,** $Rb_2O.4WO_3.8H_2O$, to be formed by mixing soln. of barium metatungstate and rubidium sulphate, and slowly cooling the concentrated filtrate. The tetragonal, octahedral crystals have the axial ratios $a : c = 1 : 0{\cdot}9702$; and the birefringence is strong and positive. The crystals lose water when exposed to air; about 7 mols. of water are given off at 150°, and all at a much higher temp. 100 parts of cold water dissolve 10 parts of the salt, but warm water dissolves much more.

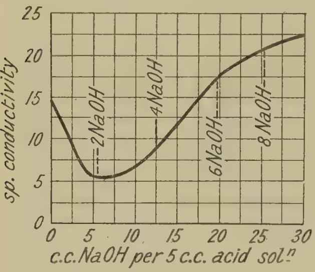


FIG. 50.—The Titration of Metatungstic Acid with Sodium Hydroxide.

C. Scheibler mixed soln. of barium metatungstate and copper sulphate, and obtained from the filtrate what were probably monoclinic plates of **copper metatungstate,** $CuO.4WO_3.11H_2O$. S. H. C. Briggs dissolved 20 grms. of tungsten trioxide in 20 c.c. of a cold, conc. aq. ammonia, and added a soln. of 5 grms. of hydrated copper sulphate in 7·5 c.c. of water and 7·5 c.c. of conc. aq. ammonia; and allowed the filtrate to stand in air. Pale blue needles of **copper hexamminometatungstate,** $CuO.4WO_3.6NH_3.8H_2O$, were formed. The salt is insoluble in water, and almost insoluble in dil. aq. ammonia. C. Scheibler mixed boiling soln. of sodium metatungstate and silver nitrate in equimolar proportions along with a couple of drops of nitric acid; filtered off the normal silver tungstate if necessary, and allowed the soln. to deposit white, octahedral crystals of **silver metatungstate,** $Ag_2O.4WO_3.3H_2O$. A. Rosenheim and F. Kohn, and C. Friedheim also prepared the salt, and found that the white, scaly crystals are almost insoluble in water; they lose 0·65 mol. of water at 110°; 0·87 mol. at 150°; 1·1 mols. at 160°; and 1·3 mols. at 200°. It is therefore assumed that at least 2, possibly 3, mols. of water are intimately associated with the molecule.

C. Scheibler obtained **calcium metatungstate,** $CaO.4WO_3.10H_2O$, from a soln. obtained by digesting hot metatungstic acid with calcium carbonate. G. N. Wyrouboff said that the crystals are triclinic pinacoids—pseudotetragonal—and have the axial ratios $a:b:c=1·0070:1:1·3694$, and $\alpha=91° 1'$; $\beta=93° 0'$; and $\gamma=90° 16'$. Twinning occurs about the (001)-plane. The birefringence is negative and feeble; and the optic axial angle $2E=115°$. C. Scheibler obtained **strontium metatungstate,** $SrO.4WO_3.8H_2O$, in a similar manner. C. Scheibler, and C. F. Rammelsberg described the crystals as tetragonal, but G. N. Wyrouboff showed that they are monoclinic prisms with the axial ratios $a:b:c=1·0556:1:0·7999$, and $\beta=90° 21'$. The birefringence is negative and feeble, and the optic axial angle $2E=93° 40'$. C. Scheibler obtained **barium metatungstate,** $BaO.4WO_3.9H_2O$, by mixing boiling conc. soln. of sodium metatungstate and barium chloride in the presence of a few drops of hydrochloric acid, and cooling. The tritungstate is also deposited as a white powder; this can be removed by levigation, or by recrystallization from water acidulated with hydrochloric acid. E. Zettnow dissolved 42 parts of sodium paratungstate, 15 parts of sodium hydrophosphate, and 15 c.c. of hydrochloric acid of sp. gr. 1·12 in 100 c.c. of water, and then added to the boiling liquid 9 parts of barium chloride. The filtrate was evaporated for crystallization, and the product recrystallized from water 2 or 3 times. L. A. Hallopeau boiled a soln. of paratungstic acid with an excess of barium carbonate, and concentrated the clear liquid in vacuo for crystallization. E. F. Smith found that the dehydration curve agreed with the formula $(BaO.WO_3)_3(H_2O.WO_3).6H_2O$. C. Scheibler, L. A. Hallopeau, and C. F. Rammelsberg described the white crystals as tetragonal octahedra, but G. N. Wyrouboff showed that they are rhombic bipyramids with the axial ratios $a:b:c=0·9962:1:1·5070$. Twinning occurs about the (110)-plane. The optic axial angle $2E=27°$; and the crystals are feebly birefringent. The sp. gr. is 4·298 at 14°. The optical character is positive; the birefringence feeble; and the optic axial angle $2E=27°$. C. Scheibler said that the crystals are stable in air; but L. A. Hallopeau, that they effloresce in air. G. N. Wyrouboff also said that the crystals lose water when exposed to air. They effloresce over conc. sulphuric acid. C. Scheibler found that the crystals lose 8·65 per cent. of water at 100°; L. A. Hallopeau, 9·27 per cent.—the theoretical loss for 6 mols. of water is 8·69 per cent. A. Rosenheim and F. Kohn found that 3 mols. of water are retained by the salt which has been heated over 100°, and that the loss of water at higher temp. is attended by diminished solubility. H. Copaux added that 1·5 mols. of water are retained at 110°, and the weight remains constant at 150°; more water is lost between 200 °and 250°, but about half a mol. is retained at 250°. After calcination the product is yellow and insoluble. The salt is freely soluble in hot water; cold water dissolves the salt with partial decomposition into barium tritungstate and free tungstic acid, but these products recombine if the liquid be heated. The addition of baryta-water to the aq. soln. precipitates normal barium tungstate.

According to C. Scheibler, on mixing soln. of barium metatungstate and silver nitrate, a liquid is obtained which furnishes aggregates of stumpy prisms of **silver barium metatungstate.**

C. Scheibler obtained a syrupy liquid by concentrating the filtrate containing **beryllium metatungstate,** obtained by double decomposition with say beryllium sulphate, and barium metatungstate. The syrup dries to a hard mass. A soln. of **magnesium metatungstate,** obtained in a similar way, furnishes monoclinic prisms of the *octohydrate*, $MgO.4WO_3.8H_2O$, which are stable in air. The axial ratios found by G. N. Wyrouboff are $a : b : c = 0{\cdot}6763 : 1 : 0{\cdot}7792$, and $\beta = 106° 43'$. The optical character is positive, and the optic axial angle $2V = 77° 50'$. Similarly with **zinc metatungstate,** $ZnO.4WO_3.10H_2O$, whose crystals are freely soluble in water. When the water is expelled by calcination at a red-heat, the residue is insoluble in water. If the soln. is crystallized between 6° and 20°, it deposits the *octohydrate*, $ZnO.4WO_3.8H_2O$, in monoclinic prismatic plates which were found by G. N. Wyrouboff to have the axial ratios $a : b : c = 0{\cdot}6626 : 1 : 0{\cdot}7557$, and $\beta = 105° 57'$. They are isomorphous with the corresponding octohydrates of magnesium and nickel metatungstates. The optical character is positive; and the optic axial angle $2H = 123°$. The corresponding **cadmium metatungstate,** $CdO.4WO_3.10H_2O$, was obtained by C. Scheibler in an analogous manner. The salt is stable in air. G. N. Wyrouboff found that the tetragonal, bipyramidal crystals have the axial ratio $a : c = 1 : 0{\cdot}9936$, and they are isomorphous with the corresponding salts of ammonium, sodium, and manganese. The birefringence is positive and strong. C. Friedheim found that the salt is stable in air; and it loses 7 mols. of water between 100° and 110°; and at a dull red-heat, 10 mols. C. Scheibler reported **mercurous metatungstate,** $Hg_2O.4WO_3.25H_2O$, to be formed by adding a soln. of mercurous nitrate to one of a soluble tungstate, or a soln. of tungstic acid; the voluminous, white precipitate becomes lemon-yellow and more compact after washing, and drying in air. C. Friedheim said that only the paratungstate is produced by this process. H. Copaux did not succeed in preparing mercurous metatungstate. Conc. soln. of metatungstic acid and mercurous nitrate give a crystalline powder whether the metatungstate or the mercurous salt be in excess, the composition of the salt is $Hg_2O : WO_3 = 1{\cdot}7 : 4$. He obtained **mercurous nitratometatungstate,** $9Hg_2O.24WO_3.N_2O_5.29H_2O$, which can be represented by the formula $H_2Hg_8[H_4(W_2O_7)_6].HgNO_3.12\frac{1}{2}H_2O$, in which the metatungstic acid has a higher basicity than is usual. G. N. Wyrouboff found that **mercuric metatungstate** prepared by double decomposition, is insoluble. A. Rosenheim and F. Kohn could not obtain a mercuric metatungstate of constant composition.

A. Rosenheim and F. Kohn prepared **thallous metatungstate,** $Tl_2O.4WO_3.3H_2O$, by mixing boiling soln. of eq. proportions of sodium metatungstate and thallous nitrate in the presence of a little nitric acid. The yellowish-white, insoluble, crystalline powder loses 2 mols. of water at 90°. C. Scheibler prepared yellow **cerous metatungstate,** $Ce_2(W_4O_{13})_3.30H_2O$, from a soln. of barium metatungstate and cerous sulphate. G. N. Wyrouboff found that the triacontahydrate is formed in triclinic prisms below 16°, and the heptacosihydrate above 16° in rhombic crystals. The triclinic crystals have the axial ratio $a : b : c = 0{\cdot}9338 : 1 : 0{\cdot}5825$, and $\alpha = 96° 43'$, $\beta = 92° 34'$, and $\gamma = 91° 30'$. The birefringence is strong. G. N. Wyrouboff similarly prepared **lanthanum metatungstate,** $La_2(W_4O_{13})_3.30H_2O$, whose triclinic crystals have the axial ratios $a : b : c = 0{\cdot}9859 : 1 : 0{\cdot}5786$, and $\alpha = 97° 6'$, $\beta = 93° 50'$, and $\gamma = 89° 2'$; and the rose-red rhombic crystals of the corresponding **didymium metatungstate,** $Di_2(W_4O_{13})_3.27H_2O$, have the axial ratios $a : b : c = 0{\cdot}9736 : 1 : 1{\cdot}2952$. The birefringence is positive and strong; and the optic axial angle $2H = 94°$. P. T. Cleve obtained **samarium metatungstate,** $Sa_2(W_4O_{13})_3.35H_2O$, by double decomposition. The crystals are soluble in water. Similarly, A. Cleve obtained **ytterbium metatungstate,** $Yb_2(W_4O_{13})_3.35H_2O$, in prismatic crystals, freely soluble in water.

J. Lefort reported **lead tetratungstate,** $3PbO.4WO_4$, to be formed by pouring a soln. of lead acetate into one of sodium tungstate, washing with water and alcohol, and drying over quicklime and sulphuric acid. The white, amorphous precipitate is stable in air. 100 parts of water dissolve 0·025 part of the salt. C. Scheibler obtained **lead metatungstate,** $PbO.4WO_3.5H_2O$, from soln. of lead acetate and metatungstic acid, or its salts, and drying the washed product in air. C. Friedheim obtained the *pentahydrate* in crystals which slowly effloresce in air, and over sulphuric acid, they lose 3·03 per cent. of water. The aq. soln. is decomposed by hydrogen sulphide; and the salt is dissolved by hot nitric acid. W. Lotz reported the hexahydrate in fine needles, to be formed by adding ammonium metatungstate to a soln. of lead nitrate, and spontaneously evaporating a soln. of the precipitate in much water. E. F. Smith said that if the mixed soln. employed by W. Lotz be not heated, but allowed to evaporate spontaneously, long silky needles of normal lead metatungstate, $PbO.4WO_3.7H_2O$, are formed. According to A. Rosenheim and F. Kohn, lead metatungstate cannot be prepared by saturating metatungstic acid with lead oxide, or by the double decomposition of an alkali metatungstate with a soln. of a lead salt. The products always have a variable composition. They found that W. Lotz's salt, as well as a similar substance obtained by V. Forcher, is **lead nitratometatungstate,** $Pb(NO_3)_2.PbW_4O_{13}.10H_2O$. The white needles lose 7 mols. of water at 100°.

C. Scheibler obtained **manganous metatungstate,** $MnO.4WO_3.10H_2O$, by double decomposition with soln. of barium metatungstate and manganous sulphate; and G. N. Wyrouboff found that the tetragonal octahedra have the axial ratio $a : c=1 : 0·9919$. The birefringence is strong and positive; and the colour by reflected light is dirty rose, and by transmitted light, amber-yellow. The crystals are isomorphous with those of the analogous sodium and cadmium salts. The salt remains unchanged in air, but loses 10·61 per cent. or 7 mols. of water at 105°. C. Scheibler found that **ferrous metatungstate** can be obtained by dissolving iron in metatungstic acid, but only impure crystals could be prepared from the soln.; while **ferric metatungstate** could not be obtained in a crystalline state. C. Scheibler obtained **cobaltous metatungstate,** $CoO.4WO_3.9H_2O$, by double decomposition with soln. of cobaltous sulphate and barium metatungstate; G. N. Wyrouboff found that the garnet-red, rhombic bipyramids have the axial ratios $a : b : c=0·9878 : 1 : 1·3764$. Twinning and trilling occur about the (110)-plane. It is isomorphous with the barium salt with which it forms solid soln. The double refraction is positive; and the optic axial angle $2E=47°$. C. Scheibler prepared **nickel metatungstate,** $NiO.4WO_3.8H_2O$, in an analogous manner; in dark green, monoclinic plates and prisms, which, according to G. N. Wyrouboff, have the axial ratios $a : b : c=0·6555 : 1 : 0·7464$, and $\beta=106° 22'$. The double refraction is positive, and the optic axial angle $2H_a=132°$.

REFERENCES.

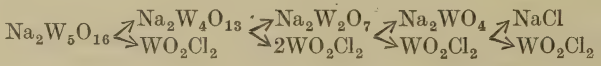
[1] F. Margueritte, *Compt. Rend.*, **20**. 294, 1845; *Journ. Pharm. Chim.*, (3), **7**. 222, 1845; *Ann. Chim. Phys.*, (3), **17**. 477, 1846; L. A. Hallopeau, *ib.*, (7), **19**. 136, 1900; E. Péchard, *ib.*, (6), **22**. 195, 1891; A. Laurent, *ib.*, (3), **21**. 62, 1847; J. Lefort, *ib.*, (5), **9**. 103, 1876; *Journ. Pharm. Chim.*, (5), **4**. 221, 1881; *Compt. Rend.*, **82**. 1182, 1876; J. Persoz, *ib.*, **58**. 1196, 1864; *Ann. Chim. Phys.*, (4), **1**. 101, 1864; J. C. G. de Marignac, *Compt. Rend.*, **55**. 888, 1862; *Ann. Chim. Phys.*, (3), **69**. 86, 1863; (4), **3**. 71, 1864; A. Riche, *ib.*, (3), **50**. 5, 1857; *Recherches sur le tungstène et ses composés*, Paris, 1857; H. Copaux, *Compt. Rend.*, **148**. 633, 1909; *Ann. Chim. Phys.*, (8), **17**. 207, 1909; (8), **26**. 32, 1912; *Zeit. anorg. Chem.*, **74**. 351, 1912; A. Rosenheim and F. Kohn, *ib.*, **69**. 247, 1911; E. Schaefer, *ib.*, **38**. 142, 1904; *Beiträge zur Kenntnis Wolframverbindungen*, Berlin, 1903; W. Lotz, *Liebig's Ann.*, **91**. 70, 1854; *Chemische Untersuchungen über die wolframsäuren Salzen*, Marburg, 1854; C. Scheibler, *Journ. prakt. Chem.*, (1), **80**. 204, 1860; (1), **83**. 304, 1861; *Chem. News*, **6**. 181, 1862; *Sitzber. Akad. Berlin*, 208, 1860; *De wolframiatibus*, Königsberg, 1861; T. M. Taylor, *Journ. Amer. Chem. Soc.*, **24**. 629, 1902; R. C. Wells, *ib.*, **29**. 112, 1907; E. F. Smith, *ib.*, **44**. 2027, 1922; *Chem. News*, **129**. 198, 207, 224, 240, 257, 286, 1924; **135**. 113, 129, 1927; G. N. Wyrouboff, *Bull. Soc. Min.*, **15**. 63, 1892; E. Zettnow, *Pogg. Ann.*, **130**. 241, 1867; A. Lottermoser, *Koll. Zeit.*, **30**. 346, 1922; C. Friedheim, *Ueber die Konstitution der Metawolframsäure und ihrer Salze*, Freiburg, 1882; C. F. Rammelsberg, *Handbuch der krystallographisch-physikalischen Chemie*, Leipzig, **1**. 579, 1881; O. Brunner,

Beiträge zur Kenntnis der Wolframbronzen, Zürich, 1903 ; V. Forcher, *Sitzber. Akad. Wien*, **44**. 164, 1862 ; *Journ. prakt. Chem.*, (1), **86**. 227, 1862 ; *Bull. Soc. Chim.*, (1), **5**. 197, 1863 ; M. Soboleff, *Zeit. anorg. Chem.*, **12**. 16, 1896 ; A. P. Sabanéeff, *ib.*, **14**. 354, 1897 ; F. Hoermann, *ib.*, **177**. 145, 1928 ; V. I. Spitzin and L. Kaschtanoff, *ib.*, **157**. 141, 1926 ; V. I. Spitzin, *ib.*, **148**. 69, 1925 ; *Journ. Russ. Phys. Chem. Soc.*, **58**. 474, 1926 ; W. Biltz and A. von Vegesack, *Zeit. phys. Chem.*, **68**. 376, 1910 ; G. Tammann, *Mém. Acad. St. Petersbourg*, (7), **35**. 1, 1887 ; G. von Knorre, *Journ. prakt. Chem.*, (2), **27**. 49, 1883 ; E. Wegelin, *Zur Kenntnis einiger Natriumwolframate*, Diessenhofen, 1906 ; C. Schoen, *Bull. Soc. Mulhouse*, **63**. 277, 1893 ; J. Eltzbacher, *Beiträge zur Elektrochemie der Wolframate*, Berlin, 11, 1899 ; N. Pappada, *Gazz. Chim. Ital.*, **32**. ii, 22, 1902 ; S. H. C. Briggs, *Journ. Chem. Soc.*, **85**. 676, 1904 ; P. T. Cleve, *Chem. News*, **53**. 93, 1886 ; *Bull. Soc. Chim.*, (2), **43**. 162, 1885 ; *Oefvers. Svenska Akad. Förh.*, **40**. 7, 1883 ; A. Cleve, *ib.*, **58**. 573, 1902 ; *Zeit. anorg. Chem.*, **32**. 152, 1902 ; *Chem. News*, **86**. 248, 1902 ; W. I. Baragiola, *Ueber das Verhalten der normalen Natrium-Kaliumsalze des Wolframs, Molybdäns, und Vanadins gegen Ammoniumchlorid*, Berlin, 1902 ; E. F. Smith, *Proc. Amer. Phil. Soc.*, **65**. 18, 1926 ; A. Wolff, *Zur Kenntnis der Parawolframate und einiger Heteropolywolframate*, Berlin, 1930 ; A. Rosenheim and A. Wolff, *Zeit. anorg. Chem.*, **193**. 47, 64, 1930 ; T. Graham, *Journ. Chem. Soc.*, **17**. 318, 1864 ; *Proc. Roy. Soc.*, **13**. 340, 1864 ; *Phil. Mag.*, (4), **28**. 314, 1864.

§ 16. The Penta- and Higher Tungstates

F. Jean[1] boiled a soln. of sodium tungstate with ammonium chloride, and obtained **ammonium pentatungstate,** $3NH_4OH.5WO_3$, as a white precipitate. The liquid, though acidic, slowly evolves ammonia. O. W. Gibbs, and J. C. G. de Marignac obtained a pentatungstate, $2(NH_4)_2O.5WO_3.5H_2O$, by dissolving ammonium paratungstate in boiling water, and cooling the soln. J. C. G. de Marignac described the crystals as triclinic pinacoids with the axial ratios $a:b:c=1{\cdot}1204:1:1{\cdot}71900$, and $\alpha=105° 46'$, $\beta=95° 17'$, and $\gamma=90° 1'$. The salt loses approximately 3·5 mols. of water at 100° ; and at ordinary temp., 100 parts of water dissolve 3·45 to 3·85 parts of salt. The aq. soln. is liable to decompose into the paratungstate and ammonia.

G. von Knorre prepared **sodium pentatungstate,** $Na_2O.5WO_3$, by fusing a mixture of a mol of sodium tungstate and two mols of tungsten trioxide, by heating sodium paratungstate to incipient fusion. On extracting the fused mass with cold water, it is left in very brilliant plates or scales. When heated for three hours with water at 150°, but little dissolves, the faintly acid liquid containing tungstate and metatungstate, the latter in by far the larger quantity. J. C. G. de Marignac occasionally obtained crystals of the henahydrate, $2Na_2O.5WO_3.11H_2O$, in the preparation of the paratungstate. The axial ratios of the monoclinic prisms are $a:b:c=0{\cdot}6056:1:0{\cdot}4477$, and $\beta=118° 36'$. J. Lefort, V. Forcher, and O. W. Gibbs seem to have obtained the same salt, which they represented $4Na_2O.10WO_3.22H_2O$, by pouring a cold, sat. soln. of normal sodium tungstate into glacial acetic acid, and washing the sparingly soluble, white, amorphous precipitate with alcohol. J. Lefort found that 100 parts of water at 15° dissolve 16 parts of the salt. O. W. Gibbs' $4Na_2O.10WO_3.23H_2O$ is probably the same salt incompletely dried ; and his $9Na_2O.22WO_3.51H_2O$, a mixture of this salt and the paratungstate. V. I. Spitzin and L. Kaschtanoff found that the action of hydrogen chloride can be represented :



$$Na_2W_5O_{16}\begin{array}{l}\nearrow Na_2W_4O_{13}\\ \searrow WO_2Cl_2\end{array}\begin{array}{l}\nearrow Na_2W_2O_7\\ \searrow 2WO_2Cl_2\end{array}\begin{array}{l}\nearrow Na_2WO_4\\ \searrow WO_2Cl_2\end{array}\begin{array}{l}\nearrow NaCl\\ \searrow WO_2Cl_2\end{array}$$

For the observations of V. I. Spitzin and others on the reduction of sodium pentatungstate, *vide supra*, tungsten bronzes. J. Lefort reported **potassium pentatungstate,** $2K_2O.5WO_3.4H_2O$, to be formed by pouring a conc. soln. of normal potassium tungstate into an excess of glacial acetic acid, and washing the white, amorphous precipitate with alcohol. Prismatic plates are formed when the cold aq. soln. is allowed to stand in a desiccator ; 100 parts of cold water dissolve 5 parts of the salt. When the salt is heated to redness, it becomes yellow and tungsten trioxide is set free. When the aq. soln. is boiled, the ditungstate and tritungstate are formed. O. W. Gibbs prepared this salt in an analogous manner, and also by mixing a cold soln. of the decatungstate with potassium bromide or nitrate; and by evaporating a soln. of normal potassium tungstate and boric acid to dryness, extracting the product with water, and allowing the soln. to crystallize. O. W. Gibbs represented the salt by the formula $4K_2O.10WO_3.9H_2O$. E. Schaefer melted a mol of rubidium carbonate with 3 to 3½ mols of tungsten trioxide and obtained a greenish mass, which was lixiviated with water acidulated with hydrochloric acid. White micaceous plates of **rubidium pentatungstate,** $Rb_2O.5WO_3$, remained. They are almost insoluble in hot water, and are decomposed by aqua regia.

O. W. Gibbs obtained **zinc pentatungstate,** $2ZnO.5WO_3.9H_2O$, which he represented by $4ZnO.10WO_3.18H_2O$, from cold soln. of sodium pentatungstate and zinc sulphate. J. Lefort mixed eq. proportions of mercuric acetate and sodium ditungstate in conc., aq. soln., and obtained a very pale yellow precipitate of **mercuric pentatungstate,** $3HgO.5WO_3.5H_2O$. It resists the action of light. 100 parts of water at 15° dissolve 0·4 part of salt. If a mixed soln. of sodium tritungstate and mercuric acetate be poured into alcohol, and the mixture allowed to stand for some hours, a white precipitate of $HgO.5WO_3.5H_2O$, is formed. It is decomposed by hot and by cold water.

According to J. Lefort, if a mixed soln. of sodium tritungstate and aluminium acetate is poured into alcohol, a white precipitate of **aluminium pentatungstate,** $Al_2O_3.5WO_3.6H_2O$, is formed. When freshly precipitated, it dissolves in water, but it soon decomposes into the tetratungstate and paratungstate. E. F. Smith and H. L. Dieck obtained **chromium pentatungstate,** $Cr_2O_3.5WO_3$, in the form of brown, rhombic needles, when eq. quantities of potassium dichromate and tungsten trioxide are heated together until the mixture fuses and no more gas is evolved. The crystals are not attacked by aqua regia; they were decomposed for analysis by fusion with sodium carbonate and potassium nitrate. J. Lefort obtained the *pentahydrate*, $Cr_2O.5WO_3.5H_2O$, by pouring into alcohol a mixed soln. of sodium tritungstate and chromic acetate. The greenish-white precipitate is considerably altered by cold and particularly by boiling water.

According to T. M. Taylor,[2] C. Scheibler's method of preparing ammonium metatungstate, *viz.*, by heating the paratungstate to 250°, furnishes a colloidal, gummy mass of **ammonium hexatungstate,** $(NH_4)_2O.6WO_3.4$ or $6H_2O$. T. M. Taylor said that to prepare this salt, the needles of the paratungstate are spread out on a watch-glass, and heated in an air-bath at 220° for one hour. The air-bath must allow the escape of water and ammonia. The product is covered with water and boiled vigorously for fifteen or twenty minutes, when a clear, but dark, heavy liquid results. This is filtered away from any residue and on evaporation dries into the gum with an almost quantitative yield. On standing several days in water, the residue will pass into the gum without previous boiling. At higher temp. considerable tungstic acid is separated and the yield is not so good. The metatungstate free from paratungstate must be heated to 250°, before yielding the gum, and the yields are nothing like so large as when the paratungstate salts are taken for the starting-out material. The yellow glass has a high index of refraction; it is miscible with water in all proportions; the aq. soln. has an acidic reaction and readily absorbs ammonia, and when neutralized with $\frac{1}{10}N$-NH_4OH, it forms the metatungstate. F. Margueritte, and A. Laurent mention the hexatungstate. A. W. Leontowitsch could not prepare F. Ullik's octotungstate but obtained instead **sodium hexatungstate,** $Na_2O.6WO_3.15H_2O$; and he obtained the same salt by dissolving 100 grms. of sodium metatungstate in 25 c.c. of water and 11·3 c.c. of hydrochloric acid of sp. gr. 1·124, and allowing the turbid soln. to stand for 4 or 5 hrs. The filtered soln. is allowed to crystallize in an ice-chamber. The sodium chloride is separated by recrystallization many times from water. The doubly refracting crystals are combinations of octahedra and hexahedra. G. Jander and co-workers also prepared $Na_6W_6O_{21}$. J. C. G. de Marignac obtained **potassium hexatungstate,** $K_2O.6WO_3.nH_2O$, as a by-product in preparing potassium metatungstate by the action of the normal tungstate on tungstic acid.

J. C. G. de Marignac obtained **sodium heptatungstate,** $Na_6W_7O_{24}.21H_2O$, by slowly cooling a soln. of sodium paratungstate which had been boiled for a long time. The triclinic pinacoids have the axial ratios $a:b:c=0·9296:1:0·5207$, and $\alpha=92° 47'$, $\beta=96° 28'$, and $\gamma=89° 40'$. The hexadecahydrate was obtained in a similar way with a soln. containing a little sodium carbonate. The triclinic pinacoids have the axial ratios $a:b:c=0·6836:1:1·1802$, and $\alpha=95° 3'$, $\beta=123° 43'$, and $\gamma=91° 53'$.

J. C. G. de Marignac[3] found that on cooling a soln. of ammonium paratungstate in boiling water, part of the unchanged salt crystallizes out, and part appears in tabular crystals of **ammonium octotungstate,** $3(NH_4)_2O.8WO_3.8H_2O$. A. Laurent obtained a similar salt. G. von Knorre obtained **sodium octotungstate,** $Na_2O.8WO_3$, by fusing sodium metatungstate or the tetratungstate, and extracting the fused mass with water. There remain scales or plates of the octotungstate, which are attacked with difficulty by acids or alkalies. F. Ullik prepared the *dodecahydrate* by mixing an aq. soln. of the metatungstate with nitric or hydrochloric acid, and spontaneously evaporating the soln. The crystals are stable in air; they are freely soluble in cold water, and the aq. soln. deposits the salt unchanged. Acids added to the aq. soln. do not give a precipitate. A. W. Leontowitsch could not prepare F. Ullik's salt but obtained instead the hexatungstate. R. C. Wells' analysis of a metatungstate gave the formula $3Na_2O.8WO_3.17H_2O$. L. A. Hallopeau treated sodium paratungstate with ammonia, dissolved the product in water, and allowed the soln. to crystallize—prismatic crystals of **ammonium sodium octotungstate,** $3\{(NH_4)Na\}_2O.8WO_3.11H_2O$, were formed. The crystals lose about 6 per cent. of water at 100°. G. von Knorre obtained steel-grey or bluish-black crystals of **potassium octotungstate,** $K_2O.8WO_3$, as a kind of tungsten bronze (*q.v.*) by electrolyzing a mixture of a mol of potassium carbonate and 3 mols of tungsten trioxide. The sp. gr. of the crystals is 6·53. E. Schaefer reported **rubidium octotungstate,** $Rb_2O.8WO_3$, by fusing a mixture of a mol of rubidium carbonate and 3 to $3\frac{1}{2}$ mols of tungstic acid, powdering the cold product, and then heating it for about three-quarters of an hour in an atm. of coal-gas. The dark-blue product can be purified by boiling it with hydrochloric acid, aqua regia, a soln. of potassium hydroxide or carbonate, and finally with water—*vide supra*, tungsten bronzes.

E. Zettnow obtained **barium octotungstate,** $BaO.8WO_3.8H_2O$, by treating a soln. of sodium paratungstate with phosphoric acid until no precipitation occurs when hydrochloric acid is added; the liquid is then acidified with hydrochloric acid, and treated with barium chloride. Most of the barium remains in soln. as metatungstate, but the remainder is precipitated as a snow-white powder of the octotungstate.

A. Riche studied the action of carbon dioxide on an aq. soln. of normal sodium tungstate, and V. Forcher found that after several days' action, small crystals of **sodium decatungstate,** $4Na_2O.10WO_3.24H_2O$, were formed. These were washed repeatedly with ice-cold water until the filtrate gave no effervescence with hydrochloric acid. J. C. G. de Marignac apparently obtained the same salt but regarded it as a pentatungstate (*q.v.*). O. W. Gibbs added that the action of acetic acid on neutral sodium tungstate is to form the 5 : 12-tungstate, the 9 : 22-tungstate, or the 4 : 10-tungstate, according to the circumstances of the case. The composition of the product depends mainly on the concentration of the acid, and the duration of its action. E. F. Smith thus described his observations:

> 100 grms. of $Na_2WO_4.2H_2O$ were dissolved in 140 c.c. of water and 50 c.c. of glacial acetic acid were gradually introduced into the soln.; the flask was cooled under running water as it became heated. Beautiful white needles separated, but on recrystallization from water the 4 : 10- and 5 : 12-salts were the products. Were the white needles not recrystallized, but simply washed with cold water, and then analyzed, the result approximated closely to the requirements of the formula $9Na_2O.22WO_3.51H_2O$. Many similar trials gave like results, which would mean that the preceding conditions gave in reality

two salts 4 : 10 and 5 : 12. Usually there was a preponderance of the first salt, the 4 : 10-salt, which J. Lefort made as a white, insoluble precipitate, by pouring a sat. soln. of the normal salt into an excess of glacial acetic acid in the cold. This was collected, washed with alcohol, and then dissolved in boiling water. On cooling, it separated in very beautiful, transparent, oblique prisms, unalterable in the air.

E. F. Smith added that the decatungstate is best made by gradually adding formic acid to a soln. of normal sodium tungstate in 100 c.c. of water until the soln. is distinctly acid, and allowing the mixture to stand for crystallization for 24 hrs. The 4 : 10-tungstate was the only product, the presence of the 5 : 12- and of the 9 : 22-tungstates was not observed. The product can be purified by recrystallization from water. The crystals are thought to be monoclinic. The sp. gr. of the salt, by E. F. Smith, is 4·3. The crystals effloresce in dry air, and when the dehydrated salt is redissolved in water much heat is evolved. V. Forcher gave $2Na_2O.5WO_3.12H_2O$ for the formula ; J. C. G. de Marignac, $2Na_2O.5WO_3.11H_2O$; and E. F. Smith, $4Na_2O.12WO_3.23H_2O$. The dehydration curve agrees with the assumption that the salt has 6 mols. of constitutional water, $4(Na_2O.WO_3).6(H_2O.WO_3).17H_2O$. V. Forcher found that the solubility of the salt is 7·94 parts per 100 parts of water at 22° ; J. Lefort, 16 per 100 at 15° ; and E. F. Smith, 19 parts per 100 at room temp. The dehydrated salt melts at 680·8°. E. F. Smith found that the addition of a cold aq. soln. of *zinc sulphate* produced a white precipitate soluble in a slight excess of zinc sulphate. From this solution, on standing, white needles separated in stellar aggregations. These were the 4 : 10-zinc salt described by O. W. Gibbs—*vide* the pentatungstates. *Cadmium sulphate* occasioned a white voluminous precipitate insoluble in an excess of cadmium sulphate as well as in cold and hot water, thus differing from the zinc salt. With *cobalt sulphate* and *nickel nitrate* precipitates soluble in an excess of the precipitants appeared. The precipitate with cobalt sulphate was quite granular. A soln. of *zirconium oxychloride* ($ZrOCl_2.8H_2O$) gave (in a soln. of the 4 : 10-salt) a heavy, white and extremely gelatinous precipitate, insoluble in water and in an excess of the precipitant. *Lanthanum sulphate* gave a white, insoluble gelatinous precipitate. This also occurred with praseodymium and neodymium nitrates. There was nothing remarkable about these products. They proved to be insoluble and were easily decomposed by nitric acid, even in the cold. *Uranyl nitrate* gave a flocculent yellow-coloured precipitate (with the 4 : 10-salt). It redissolved in a slight excess of the uranyl salt. The soln. was filtered, when a white, granular powder separated. *Ferric ammonium sulphate* gave a curdy, slightly yellow precipitate, insoluble in an excess of the precipitant. *Alum* produced a copious, finely-divided precipitate, which curdled on agitation. It proved perfectly insoluble. *Chromium potassium sulphate* occasioned a precipitate. It was greenish-grey in colour, gelatinous and insoluble in excess of the reagent and also in large volumes of water. *Lead nitrate* produced a white, gelatinous precipitate, insoluble in an excess of the precipitant and also in hot water. *Hydroxylamine hydrochloride* (in a soln. of 4 : 10-salt) caused no precipitation. With *hydrazine sulphate* a rather voluminous, somewhat flocculent, white precipitate appeared, insoluble in cold water, but dissolving rather freely in hot water, and was not soluble in an excess of hydrazine sulphate. *Benzidine hydrochloride* produced a white, heavy precipitate not soluble in an excess of the precipitant or in boiling water. *Phenylhydrazine hydrochloride* was without visible reaction. *Naphthylamine hydrochloride* gave a flesh-coloured precipitate, insoluble even in boiling water. Hydrochloric acid slowly decomposed it. *Aniline hydrochloride* gave no precipitation.

O. W. Gibbs[4] found that a mixed soln. of sodium pentatungstate and ammonium chloride, furnished white, talc-like scales of **ammonium sodium decatungstate,** $16(NH_4)_2O.4Na_2O.50WO_3.50H_2O$, or $4\{4(NH_4)_2O.10WO_3\}.4Na_2O.10WO_3.50H_2O$. W. I. Baragiola obtained **ammonium sodium 3 : 1-decatungstate,** $3(NH_4)_2O.Na_2O.10WO_3.12H_2O$, from a hot, sat. soln. of a mol of sodium tungstate and 2 mols of ammonium chloride. It is either an isomorphous mixture, or a salt

$NaO.WO_2.O.WO(O.WO_2.ONH_4)_3$. E. F. Smith prepared **calcium decatungstate,** $4CaO.10WO_3.25H_2O$, as a white, granular powder which did not melt at a low red-heat; similarly also with **strontium decatungstate,** $4SrO.10WO_3.26H_2O$, and barium decatungstate, $4BaO.10WO_3.22H_2O$; **zinc decatungstate,** $4ZnO.10WO_3.29H_2O$—*vide supra*, the pentatungstates; **manganese decatungstate,** $4MnO.10WO_3.30H_2O$, appears as a white precipitate; **cobalt decatungstate,** $4CoO.10WO_3.35H_2O$, is pink, and insoluble; and **nickel decatungstate,** $4NiO.10WO_3.34H_2O$, is a greenish-white powder. A. Wolff prepared **potassium ferric decatungstate,** $3K_2O.Fe_2O_3.10WO_3.23H_2O$.

A. Rosenheim and H. Schwer[5] prepared **ammonium ferric dodecatungstate,** $4(NH_4)_2O.Fe_2O_3.12WO_3.23H_2O$, which they represented by the formula $(NH_4)_4H_5[Fe(WO_4)_6].9H_2O$. Ferric chloride soln. was added in small portions at a time to a boiling soln. of sodium paratungstate. The brown precipitate first produced redissolves in the liquid. Ammonium chloride was added to saturation. On cooling the soln., a pale yellow, microcrystalline precipitate separated out. By using potassium chloride in place of ammonium chloride, **potassium ferric dodecatungstate,** $K_4H_5[Fe(WO_4)_6].9H_2O$, was similarly obtained. When the salt is heated nine mols. of water are expelled more readily than the remainder. Thus, at 120°, 8·8 mols. were given off; similarly at 130°; at 140°, 8·9 mols. were given off; at 160°, 9·3 mols.; and at a red-heat, 11·5 mols. The eq. conductivity of a soln. of an eq. of $K_4H_5[Fe(WO_4)_6].9H_2O$ in v litres of water at 25° was:

v . .	32	64	128	256	512	1024
λ . .	78·13	88·36	97·27	105·65	116·7	125·9

from which it follows that $\lambda_{1024}-\lambda_{32}=47{\cdot}8$. The sp. conductivities of $\frac{1}{64}N$-$\{K_4H_5[Fe(WO_4)_6].9H_2O\}$ with additions of 0, 1, and 2 eq. of $\frac{1}{10}N$-NaOH, are respectively 1·349, 1·562, and 1·704 mhos, and with more of the soda-lye, ferric hydroxide separates out. All this is taken to mean that an enneabasic ferritungstic acid is involved, resembling the corresponding ferrimolybdic acid. The anion is unstable towards hydroxyl ions so that acids of higher basicity are scarcely possible. The tetrabasic potassium salt is ionized approximately the same as an ordinary "neutral salt." A guanidinium salt, $(CH_6N_3)_3H_6[Fe(WO_4)_6].9H_2O$, has been prepared—*vide supra*, paratungstates.

G. von Knorre[6] fused potassium paratungstate, or a mixture of a mol of the normal tungstate with one or two mols of tungsten trioxide, and extracted the mass with water. Crystals of **potassium tetradecatungstate,** $5K_2O.14WO_3$, remained. They are very sparingly soluble in cold water, and rather more soluble in hot water.

W. I. Baragiola[7] obtained **ammonium sodium 3 : 2-pentadecatungstate,** $3(NH_4)_2O.2Na_2O.15WO_3.25H_2O$, in white plates from a soln. of 2 mols of ammonium chloride and a mol of sodium tungstate after the decatungstate has separated out. A hot, sat. soln. of 2 mols of ammonium chloride and one mol of sodium tungstate furnishes crystals of **ammonium sodium 4 : 2-pentadecatungstate,** $4(NH_4)_2O.2Na_2O.15WO_3.21H_2O$.

J. C. G. de Marignac[8] obtained **ammonium hexadecatungstate,** $3(NH_4)_2O.16WO_3.17H_2O$, by the spontaneous evaporation of a soln. of the metatungstate mixed with some hydrochloric acid. The crystals are probably triclinic, and they lose about 13 mols. of water at 100°. The aq. soln. has an acid reaction; and on crystallizing the aq. soln., the metatungstate separates out first. O. W. Gibbs, and G. von Knorre prepared **ammonium sodium hexadecatungstate,** $4(NH_4)_2O.3Na_2O.16WO_3.18H_2O$. G. Jander and co-workers prepared **arsenic octodecatungstic acid,** $H_8[As(W_2O_7)_9]$.

As indicated in connection with the decatungstates, O. W. Gibbs[9] prepared a complex **sodium docositungstate,** $5Na_2O.12WO_3.5Na_2O.10WO_3.51H_2O$, or $9Na_2O.22WO_3.51H_2O$, in following the directions of C. Scheibler for preparing the paratungstate, and he added that this salt is produced in crystals if the proportion of hydrochloric acid is just sufficient to give a wine-red reaction with litmus. E. F. Smith found the dehydrated salt melts at 683·3°. He obtained this salt, but doubted its individuality. By treatment with zinc sulphate, **zinc docositungstate,** $9ZnO.22WO_3.66H_2O$, is formed.

REFERENCES.

[1] F. Jean, *Compt. Rend.*, **78**. 1436, 1874; J. C. G. de Marignac, *Ann. Chim. Phys.*, (3), **69**. 60, 1863; (4), **3**. 74, 1864; O. W. Gibbs, *Proc. Amer. Acad.*, **15**. 1, 1879; *Amer. Chem. Journ.*, **1**. 2, 218, 1879; E. Schaefer, *Beiträge zur Kenntnis der Wolframverbindungen*, Berlin, 1903; *Zeit. anorg. Chem.*, **38**. 143, 1904; J. Lefort, *Compt. Rend.*, **88**. 798, 1879; *Ann. Chim. Phys.*, (5), **17**. 479, 1879; E. F. Smith and H. L. Dieck, *Zeit. anorg. Chem.*, **5**. 13, 1893; V. I. Spitzin, *Journ. Russ. Phys. Chem. Soc.*, **58**. 474, 1926; *Zeit. anorg. Chem.*, **148**. 69, 1925; V. I. Spitzin and L. Kaschtanoff, *ib.*, **157**. 141, 1926; G. von Knorre, *Journ. prakt. Chem.*, (2), **27**. 49, 1883; V. Forcher, *Sitzber. Acad. Wien*, **44**. 164, 1862; *Journ. prakt. Chem.*, (1), **86**. 227, 1862; *Bull. Soc. Chim.*, (1), **5**. 197, 1863.

[2] F. Margueritte, *Compt. Rend.*, **20**. 294, 1845; *Journ. Pharm. Chim.*, (3), **7**. 222, 1845; *Ann. Chim. Phys.*, (3), **17**. 477, 1846; A. Laurent, *ib.*, (3), **21**. 62, 1847; J. C. G. de Marignac, *ib.*, (3), **69**. 33, 1863; T. M. Taylor, *Journ. Amer. Chem. Soc.*, **24**. 629, 1902; C. Scheibler, *Journ. prakt. Chem.*, (1), **83**. 604, 1861; A. W. Leontowitsch, *Journ. Russ. Phys. Chem. Soc.*, **37**. 130, 1905; F. Ullik, *Sitzber. Akad. Wien*, **56**. 157, 1867; G. Jander, D. Mojert and T. Aden, *Zeit. anorg. Chem.*, **180**. 129, 1929.

[3] J. C. G. de Marignac, *Ann. Chim. Phys.*, (3), **69**. 32, 1863; A. Laurent, *ib.*, (3), **21**. 62, 1847; L. A. Hallopeau, *ib.*, (7), **19**. 96, 1900; G. von Knorre, *Journ. prakt. Chem.*, (2), **27**. 49, 1883; F. Ullik, *Sitzber. Akad. Wien*, **56**. 157, 1867; R. C. Wells, *Journ. Amer. Chem. Soc.*, **29**. 112, 1907; E. F. Smith, *ib.*, **44**. 2027, 1922; *Chem. News*, **129**. 198, 207, 224, 257, 286, 1924; O. W. Gibbs, *Proc. Amer. Acad.*, **15**. 1, 1880; *Amer. Chem. Journ.*, **1**. 2, 218, 1879; A. W. Leontowitsch, *Journ. Russ. Phys. Chem. Soc.*, **37**. 130, 1905; E. Schaefer, *Beiträge zur Kenntnis der Wolframverbindungen*, Berlin, 1903; *Zeit. anorg. Chem.*, **38**. 143, 1904; E. Zettnow, *Pogg. Ann.*, **130**. 247, 1867; A. Riche, *Ann. Chim. Phys.*, (3), **50**. 5, 1857; J. Lefort, *ib.*, (5), **9**. 97, 1876; *Compt. Rend.*, **88**. 798, 1879; V. Forcher, *Sitzber. Akad. Wien*, **44**. 165, 1861; *Bull. Soc. Chim.*, (2), **5**. 97, 1863; *Journ. prakt. Chem.*, (1), **86**. 240, 1862; G. von Knorre, *ib.*, (2), **27**. 84, 1883; C. Gonzales, *ib.*, (2), **36**. 47, 1887; J. C. G. de Marignac, *Ann. Chim. Phys.*, (3), **69**. 60, 1863; (4), **3**. 74, 1864.

[4] O. W. Gibbs, *Proc. Amer. Acad.*, **15**. 1, 1880; *Amer. Chem. Journ.*, **1**. 2, 218, 1879; W. I. Baragiola, *Ueber das Verhalten der normalen Natrium-Kaliumsalze des Wolframs, Molybdäns, und Vanadins gegen Ammoniumchlorid*, Berlin, 1902; E. F. Smith, *Journ. Amer. Chem. Soc.*, **44**. 2027, 1922; *Chem. News*, **129**. 198, 207, 224, 257, 286, 1924; A. Wolff, *Zur Kenntnis der Parawolframate und einiger Heteropolywolframate*, Berlin, 1930; A. Rosenheim and A. Wolff, *Zeit. anorg. Chem.*, **193**. 47, 64, 1930.

[5] A. Rosenheim and H. Schwer, *Zeit. anorg. Chem.*, **89**. 229, 1914.

[6] G. von Knorre, *Journ. prakt. Chem.*, (2), **27**. 49, 1883.

[7] W. I. Baragiola, *Ueber das Verhalten der normalen Natrium-Kaliumsalze des Wolframs, Molybdäns, und Vanadins gegen Ammoniumchlorid*, Berlin, 1902.

[8] J. C. G. de Marignac, *Ann. Chim. Phys.*, (4), **3**. 75, 1864; O. W. Gibbs, *Amer. Chem. Journ.*, **7**. 236, 1886; G. von Knorre, *Ber.*, **19**. 823, 1886; G. Jander, D. Mojert and T. Aden, *Zeit. anorg. Chem.*, **180**, 129, 1929.

[9] O. W. Gibbs, *Proc. Amer. Acad.*, **15**. 1, 1880; *Amer. Chem. Journ.*, **1**. 2, 218, 1879; C. Scheibler, *Journ. prakt. Chem.*, (1), **80**. 204, 1860; (1), **83**. 273, 1861; *Chem. News*, **6**. 181, 1862; *Sitzber. Akad. Berlin*, 208, 1860; E. F. Smith, *Journ. Amer. Chem. Soc.*, **44**. 2027, 1922; *Chem. News*, **129**. 198, 207, 224, 240, 257, 286, 1924.

§ 17. The Pertungstic Acids and the Pertungstates

According to T. Fairley,[1] hydrogen dioxide dissolves tungsten trioxide forming a soln. containing an unstable higher oxide from which green, scaly crystals are deposited on evaporation over sulphuric acid in vacuo; this product is soluble in water, and forms unstable, crystalline compounds with the alkali dioxides. J. B. Cammerer treated tungsten trioxide with a boiling, two per cent. soln. of hydrogen dioxide, and on evaporating the soln. he obtained a deep orange, amorphous mass of **monopertungstic acid,** $H_2WO_5.H_2O$, or $WO_3.H_2O_2.H_2O$, which dissolves in water, and the soln. has an acidic reaction. B. Kellner could not isolate a product of definite composition from a soln. of hydrated tungstic acid in hydrogen dioxide. When the soln. is concentrated, it decomposes when heated, although the dil. soln. does not decompose when boiled at 100°. No precipitation occurs when alcohol or ether is added. If evaporated in a desiccator, an amorphous substance approximating **perditungstic acid,** $H_2W_2O_8.2H_2O$, or $W_2O_7.3H_2O$, is formed. It decomposes at about 35°. It decomposes in water with the evolution of oxygen; L. Pissarjewsky was unable to prepare this compound; but he inferred from his observations on the thermal value, *Q* Cals., of the reaction between tungsten trioxide and hydrogen dioxide that such a compound probably exists but is less stable than that between hydrogen dioxide and molybdenum trioxide (*q.v.*):

Mols H_2O_2 per mol WO_3	1	2	3	4	5	6	10
Heat developed, *Q* .	0·89	1·536	2·001	2·728	3·233	3·335	3·466 Cals.

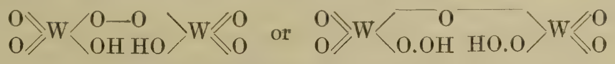
J. Brode's observations on the distribution of hydrogen dioxide between ether and aq. soln. of tungstic acid, at 20°, confirm the view that if monopertungstic acid exists in aq. soln., it is even more dissociated in aq. soln. than is the case with the corresponding monopermolybdic acid. Thus, with soln. containing $\frac{1}{2}M$-Na_2WO_4 and $\frac{1}{8}M$-H_2SO_4:

Free H_2O_2 . . .	0·265	0·200	0·097 mol
Bound H_2O_2 per mol WO_3 .	1·34	1·13	0·77 mol

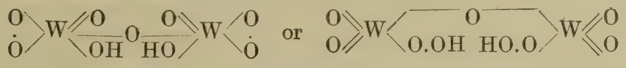
L. Pissarjewsky assumed that the soln. contained monopertungstic acid, $WO_2(OH)(OOH)$, and dipertungstic acid, $WO_2(OOH)_2$, in equilibrium: $nWO_2(OOH)_2+(n+m)H_2O \rightleftharpoons (n-m)WO_2(OOH)(OH)+mWO_2(OH)_2+(n+m)H_2O_2$. He calculated the heat of formation of H_2WO_5 in soln. from tungstic acid and oxygen to be −18·154 Cals. A. Mazzucchelli and C. Barbero found the potential of a gram-equivalent of sodium pertungstate in 10 litres of N-H_2SO_4, against a $Hg : Hg_2SO_4 : N$-H_2SO_4-electrode, after 1, 4, and 15 hrs., to be respectively −0·891, −0·881, −0·865 volt with a large platinum electrode; −0·894, −0·886, −0·865 volt with a small platinum electrode; and −0·970, −0·952, and −0·947 volt with a gold electrode. A. Mazzucchelli and M. Borghi studied the formation of complexes with optically active organic substances. E. P. Alvarez studied the action of the pertungstates on soln. of lead acetate (white precipitate), silver nitrate (white precipitate), mercurous nitrate (white precipitate, with rapid decomposition), mercuric chloride (red precipitate), copper sulphate (blue precipitate), zinc and cadmium sulphates (white precipitates), bismuth nitrate (white precipitate), gold chloride (slight effervescence and escape of oxygen), manganous chloride (pink precipitate), nickelous chloride or sulphate (greenish-white precipitate), cobaltous nitrate and chloride (pink precipitate), ferrous sulphate (green or bluish-green precipitate), ferric chloride (red ferric hydroxide), and alkaline earth chlorides (white precipitates). The precipitates are all per-salts of the bases in question.

According to E. Péchard, when a soln. of sodium paratungstate is boiled for a few minutes with hydrogen dioxide, it assumes a yellow tint, and no longer gives a precipitate with nitric acid; when it is evaporated in vacuo, the syrupy liquid deposits small, white, radiating crystals of $Na_2O.W_2O_7.2H_2O$, that is, **sodium monoperditungstate,** $Na_2W_2O_8.2H_2O$. He also prepared **ammonium monoperditungstate,** in a similar manner, but B. Kellner could not isolate an ammonium pertungstate. E. Péchard added that sodium perditungstate is more soluble in water than sodium paratungstate; it gives off water when heated in vacuo, and finally decomposes with the evolution of oxygen. Alkali-lye destroys these salts with the liberation of oxygen; and aq. soln. liberate iodine from potassium iodide, and chlorine from hydrochloric acid. G. E. Thomas found that by electrolyzing a 30 per cent. soln. of sodium tungstate slightly acidified with acetic acid, sodium pertungstate is formed, but he did not isolate the salt; but J. Eltzbacher could not prepare sodium pertungstate by the electrolysis of a soln. of the normal tungstate using a high anodic current density. B. Kellner could not prepare E. Péchard's hydrate, but he obtained crystals of the *tetrahydrate*, $Na_2W_2O_8.4H_2O$, belonging to the rhombic system, by the action of hydrogen dioxide on an acid soln. of sodium paratungstate mixed with a little sodium tungstate so that the soln. would not react acid. A. Mazzucchelli and C. Barbero found the electrode potentials towards the normal calomel electrode with soln. of sodium perditungstate, $Na_2W_2O_8.6H_2O$, after 1, 3, and 7 hrs. to be respectively —0·746, —0·733, and —0·733 volt with large platinum electrodes; —0·729, —0·736, and —7·730 volt with small platinum electrodes; and —0·699, —0·687, and —0·699 volt with gold electrodes. Hydrogen dioxide does not dissolve silver paratungstate, and it is decomposed by normal silver tungstate; but **silver perditungstate,** $Ag_2W_2O_8.4H_2O$, was obtained by adding silver nitrate to a soln. of potassium pertungstate. The white precipitate is sparingly soluble in water. B. Kellner also prepared **strontium perditungstate,** $SrW_2O_8.6H_2O$, by adding an excess of strontium nitrate to a soln. of potassium hypertungstate containing a little hydrogen dioxide; and similarly with **barium perditungstate,** $BaW_2O_8.6H_2O$.

L. Pissarjewsky prepared a salt with the composition, **sodium perditungstate,** $Na_2W_2O_9.6H_2O$, by warming sodium paratungstate for 10 minutes with an excess of hydrogen dioxide, precipitating the salt by the addition of alcohol, and recrystallizing from water. The white powder has a yellow tinge, and it consists of microscopic, rhombic prisms. It deliquesces a little in air, and with dil. sulphuric acid it forms hydrogen dioxide, and with conc. sulphuric acid, ozone. B. Kellner obtained white rhombic crystals of **lithium perditungstate,** $Li_2W_2O_9.6H_2O$, by adding a soln. of lithium sulphate to a soln. of ammonium paratungstate in hydrogen dioxide. The salt is sparingly soluble in water. According to L. Pissarjewsky, the ratio of WO_3 to active oxygen in $Na_2W_2O_8.2H_2O$ is 2 : 1, and in $Na_2W_2O_9.6H_2O$, 1 : 1, when determined by titration with potassium permanganate in sulphuric acid soln. Hence, by analogy with the persulphates, the constitutions of the acids corresponding with these two salts may be represented:

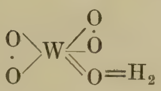


Monoperditungstic Acid, $H_2W_2O_8$

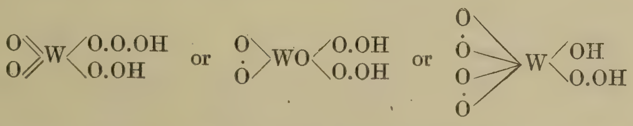


Diperditungstic Acid, $H_2W_2O_9$

so that L. Pissarjewsky's acid can be regarded as a condensation product of two molecules of H_2WO_5, *i.e.*

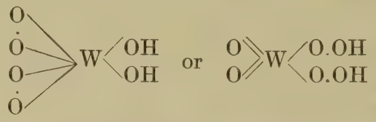


with the expulsion of a mol. of water. P. G. Melikoff and L. Pissarjewsky also prepared a peroxidized salt of this acid, namely, **sodium dipertungstate,** $Na_2O_2.WO_4.H_2O_2$, or $Na_2O_2.WO_5.H_2O$, which can be regarded as a derivative of *dipertungstic acid,* H_2WO_7, or

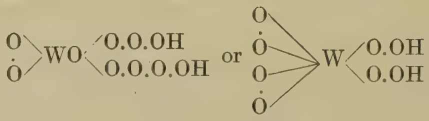


The salt was prepared by the action of a well-cooled soln. of sodium hydroxide (1½ mol NaOH to one mol of $NaWO_4$) and hydrogen dioxide (six times the calculated quantity) on a soln. of perditungstate. The yellow powder slowly decomposes with the evolution of oxygen; when warmed it decomposes with a feeble detonation; and when treated with water, the evolution of oxygen is attended by effervescence.

Iodine is liberated from potassium iodide ; and with conc. sulphuric acid ozone is given off, and with dil. sulphuric acid, hydrogen dioxide is formed. By cooling to —2° a soln. of 3 mols of sodium hydroxide, half a mol of $Na_2W_2O_8$, and an excess of hydrogen dioxide, P. G. Melikoff and L. Pissarjewsky obtained a yellow complex $(Na_2O_2)_2WO_4(Na_2O_2.WO_4.H_2O_2).7H_2O$, which behaves chemically like the preceding salt. E. Wegelin reported sodium dipertungstate, $Na_2WO_6.4H_2O$, or $Na_2WO_4.2H_2O_2.2H_2O$, a derivative of dipertungstic acid, H_2WO_6 :



to be formed by cooling a soln. of normal sodium tungstate with an excess of 25 per cent. hydrogen dioxide. The white, crystalline powder has a yellow tinge ; it gives off oxygen when dissolved in water. The salt also exhibits the general properties of the pertungstates. P. G. Melikoff and L. Pissarjewsky prepared **potassium hypertungstate,** $K_2O_4.WO_4.H_2O$, derived from the acid



or, if the water of crystallization be included in the formula, and pertungstic acid be represented $WO(OOH)_4$, the potassium salt becomes $WO(OOK)_2(OOH)_2$. It was obtained by adding an excess of hydrogen dioxide to a well-cooled soln. of potassium hydroxide and tungstate, and precipitating the salt by the addition of alcohol. The pale yellow precipitate decomposes in air ; it explodes by friction, or by rapidly heating it to 80° ; if slowly heated, oxygen is given off. When treated with water, oxygen is given off ; and the salt gives other reactions characteristic of the pertungstates. B. Kellner prepared hexagonal prisms of **potassium hyperditungstate,** $K_2W_2O_{11}.4H_2O$, from a soln. of potassium paratungstate and cold 20 per cent. hydrogen dioxide. The salt is stable ; and it is precipitated from its aq. soln. by a mixture of alcohol and ether. Most salts of the heavy metals give precipitates with the aq. soln.—*e.g.* barium, lead, mercuric, and silver nitrates, and thallosic sulphate.

B. Kellner obtained **lithium pertetratungstate,** $Li_6W_4O_{16}.9H_2O$, in hexagonal crystals, from the mother-liquor in the preparation of the diperditungstate. He also prepared **rubidium pertetratungstate,** $Rb_4W_4O_{15}.3H_2O$, in stable, rhombic plates by evaporating the filtrate from a soln. of rubidium paratungstate in an excess of 20 per cent. hydrogen dioxide ; and white crystals of **magnesium pertetratungstate,** $Mg_2W_4O_{20}.9H_2O$, from a soln. of magnesium paratungstate in an excess of 20 per cent. hydrogen dioxide. B. Kellner reported **calcium perhexatungstate,** $Ca_3W_6O_{27}.8H_2O$, to be formed, as a white precipitate, by adding calcium nitrate to a soln. of sodium paratungstate and normal tungstate in an excess of hydrogen dioxide. If potassium hypertungstate is dissolved in 10 to 15 times its weight of cold water, and the soln. allowed to stand overnight, rhombic crystals of **potassium perdecatungstate,** $K_{14}W_{30}O_{52}.22H_2O$, are formed. If cæsium sulphate be added to a hot soln. of 5 mols of sodium paratungstate and 2 mols of the normal sulphate in an equal weight of 20 per cent. hydrogen dioxide, on cooling, a microcrystalline precipitate of **cæsium perdodecatungstate,** $Cs_6W_{12}O_{41}.12H_2O$, is formed. An excess of a soln. of cæsium sulphate added to a hot soln. of sodium paratungstate in 1·2 to 1·4 times its weight of 15 per cent. hydrogen dioxide, yields yellow crystals of **cæsium perparatungstate,** $Cs_{10}W_{12}O_{65}.11H_2O$; and rubidium sulphate similarly furnishes **rubidium perparatungstate,** $Rb_{10}W_{12}O_{44}.12H_2O$, as a microcrystalline powder. These salts want overhauling.

REFERENCES.

[1] T. Fairley, *Journ. Chem. Soc.*, **31**. 127, 1877; J. B. Cammerer, *Chem. Ztg.*, **15**. 957, 1891; E. Péchard, *Compt. Rend.*, **112**. 1060, 1891; J. Brode, *Zeit. phys. Chem.*, **37**. 299, 1901; L. Pissarjewsky, *ib.*, **43**. 160, 1903; *Journ. Russ. Phys. Chem. Soc.*, **32**. 155, 1900; **34**. 472, 1902; **35**. 42, 1903; *Zeit. anorg. Chem.*, **18**. 59, 1898; **24**. 108, 1900; **32**. 341, 1902; P. G. Melikoff and L. Pissarjewsky, *ib.*, **18**. 59, 1898; *Ber.*, **31**. 632, 1898; A. Mazzucchelli and C. Barbero, *Atti Accad. Lincei*, (5), **15**. ii, 35, 109, 1906; A. Mazzucchelli and M. Borghi, *Gazz. Chim. Ital.*, **40**. ii, 241, 1910; E. P. Alvarez, *Chem. News*, **94**. 269, 1906; *Ann. Chim. Anal. Appl.*, **11**. 401, 1896; G. E. Thomas, *Journ. Amer. Chem. Soc.*, **21**. 373, 1899; E. Wegelin, *Zur Kenntnis einiger Natriumwolframate*, Zürich, 1906; B. Kellner, *Untersuchungen über Perwolframate*, Berlin, 1909; J. Eltzbacher, *Beiträge zur Elektrochemie der Wolframate*, Berlin, 1899.

§ 18. Tungsten Fluorides and Oxyfluorides

According to H. Moissan,[1] fluorine at ordinary temp. attacks tungsten with incandescence forming a volatile fluoride. J. J. Berzelius observed that while tungsten trioxide which has been ignited dissolves sparingly in hydrofluoric acid, hydrated tungsten trioxide forms with hydrofluoric acid a yellow, milky liquid, which is soluble in a large proportion of water. On evaporation, the soln. yields a yellow syrup, which, at a higher temp., loses some acid and solidifies to a greenish mass. The product is not decomposed by ignition in a closed vessel, and redissolves imperfectly in water to form a milky liquid as before; while the insoluble part retains hydrofluoric acid so very tenaciously that it can be expelled only by ignition with lumps of ammonium carbonate. The salts obtained by J. J. Berzelius were probably fluodioxytungstates—*vide infra*. A. Riche said that hydrated tungsten trioxide dissolves in conc. hydrofluoric acid at 50° to 60°, but on evaporating the soln. in air, crystals of hydrated tungsten trioxide separate out.

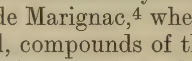
A. Rosenheim and T. H. Li[2] obtained complex salts of **tungsten trifluoride,** WF_3, namely, **ammonium tungsten tetrafluoride,** $(NH_4)WF_4.H_2O$; and **potassium tungsten tetrafluoride,** $KWF_4.H_2O$—*vide infra*, tungsten trichloride.

O. Ruff and co-workers[3] obtained **tungsten hexafluoride,** WF_6, by the action of anhydrous hydrogen fluoride on tungsten hexachloride in a copper-lined bomb at ordinary temp. The gas is passed over titanium tetrafluoride to absorb the excess of hydrogen fluoride, and then into a platinum vessel, or a paraffin-lined vessel, cooled to —70°, at which temp. the product is solid. Tungsten hexafluoride is also formed by the interaction of the hexachloride and arsenic trifluoride, but even repeated fractionation does not quite free the product from arsenic trifluoride. The most convenient mode of preparation is gradually to add antimony pentafluoride to tungsten hexachloride, cooled by a freezing mixture, and subsequently to distil the product. Glass vessels can be used. The yield is 60 to 80 per cent. Tungsten hexafluoride is a colourless gas at ordinary temp. It is ten times as heavy as air, and is the heaviest of all known gases. At atm. press., it condenses at the b.p., 19·5° to a pale yellow liquid, and below the m.p. 2·5° it forms a white solid. The vap. press. at 2·5° is 375 mm.; at 15°, 649 mm.; at 19°, 751 mm.; and at 19·5°, 760 mm. It vaporizes without melting at —20° under 380 mm. press., and at 0° under 760 mm. press. The vapour density at 18·5° is 303—theory 298. The compound fumes strongly in air forming a bluish-white cloud. It is decomposed by water with the separation of yellow, hydrated tungsten trioxide. The gas is freely soluble in aq. alkalies, and aq. ammonia; and it is absorbed by alkali fluorides forming complex salts. Ammonia gas reacts vigorously forming a brown solid; while liquid ammonia in a closed vessel forms ammonium fluoride and a clear soln. which on evaporation leaves a white solid. Tungsten hexafluoride, particularly if it contains traces of hydrogen fluoride, rapidly attacks copper, zinc, mercury, tin, lead, antimony, iron, cobalt, and nickel, the metal so acquires a blue or grey film. Gold and platinum are not attacked by tungsten hexafluoride.

O. Ruff and co-workers prepared **tungsten oxytetrafluoride,** WOF_4, by the interaction of equal amounts of the oxytetrachloride and anhydrous hydrogen fluoride in a platinum vessel at 20°, and then allowing the temperature to rise gradually. After 24 hrs., the vessel is heated to 280°, while the upper part is kept cool. The oxytetrafluoride condenses in the neck as a snow-white mass. It has also been obtained by the action of lead or bismuth fluoride on tungsten trioxide, while moisture is carefully excluded. At ordinary temp., the oxytetrafluoride forms colourless, hygroscopic plates; its m.p. is 110°, and its b.p. 185° to 190°. It is coloured yellow in moist air owing to the separation of hydrated tungsten trioxide; it forms a clear soln. with water while generating much heat, hydrogen fluoride is given off, and the soln. soon deposits hydrated tungsten trioxide. Hydrogen sulphide attacks it superficially, with partial reduction to a blue substance. It absorbs ammonia in the cold forming **tungsten hemiamminoxytetrafluoride,** $2WOF_4.NH_3$. This substance is orange coloured; it acquires a white crust on exposure to air; it melts when heated giving off hydrogen fluoride and ammonium fluoride, and leaving a residue of blue tungsten trioxide; when heated in ammonia, it detonates slightly; it is insoluble in liquid ammonia; it dissolves in water and acquires a blue colour; and the aq. soln. remains clear for some time, but slowly deposits hydrated tungsten trioxide. Tungsten oxytetrafluoride is insoluble in carbon tetrachloride, but soluble in carbon disulphide, chloroform, and absolute alcohol; it is sparingly soluble in dry benzene, and with moist benzene the tungsten is partly reduced; it is slightly soluble in ether with the development of heat; and in acetic anhydride with partial decomposition. It does not attack in the cold copper, silver, zinc, tin, lead, aluminium, arsenic, bismuth, and iron, but when heated, or when moist, the metal acquires a blue film.

Attempts by O. Ruff and co-workers to prepare **tungsten dioxydifluoride,** WO_2F_2, were not successful, although this compound mixed with the oxytetrafluoride results when tungsten trioxide and lead fluoride are heated in the presence of a trace of moisture; and a little is formed by the action of water on the oxytetrafluoride. According to J. C. G. de Marignac,[4] when the normal or meta-tungstates are dissolved in hydrofluoric acid, compounds of the metal fluorides with tungsten dioxydifluoride—**fluodioxytungstates**—are formed. The salts are usually soluble in water, and they crystallize readily. The dry salts attack glass. Acids do not produce a precipitate in aq. soln., but the soln. slowly deposits hydrated tungsten trioxide. Some reactions of soln. of these salts were described by R. D. Hall and E. F. Smith—*vide* Table III, **9.** 55, 4.

J. C. G. de Marignac prepared **ammonium trifluodioxytungstate,** $NH_4F.WO_2F_2.H_2O$, or, according to A. Werner, $NH_4[WO_2F_3(H_2O)]$, by the action of hydrofluoric acid on ammonium paratungstate; the exact conditions are not known because often the tetrafluodioxytungstate and tungsten trioxide are produced. The rhombic bipyramids have the axial ratios $a:b:c=0{\cdot}5224:1:0{\cdot}7268$. Some combinations are pseudohexagonal; and twinning like aragonite may occur. F. Mauro discussed the isomorphism of the salt. The salt is decomposed by water, but can be crystallized unchanged from water containing hydrofluoric acid. J. C. G. de Marignac also prepared rectangular plates of **ammonium tetrafluodioxytungstate,** $2NH_4F.WO_2F_2.H_2O$, which A. Werner formulated $(NH_4)_2[WO_2F_4]$; and J. W. Mallet



$$\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\!\gg\mathrm{W}\!<\!\begin{matrix}\mathrm{F:F.NH_4}\\ \mathrm{F:F.NH_4}\end{matrix}$$

The salt was obtained from a soln. of ammonium tungstate in hydrofluoric acid. The rhombic bipyramids have the axial ratio $a:b:c=0{\cdot}4128:1:1{\cdot}0027$. F. Mauro, and E. Scacchi found the salt to be isomorphous with $2NH_4F.MoO_2F_2$, and $2NH_4F.MoOF_3$. J. J. Berzelius seems to have prepared this salt as well as the corresponding potassium compound—*vide supra*. J. C. G. de Marignac found that ammonium tetrafluodioxytungstate does not change at 100°, and at a higher temp. it decomposes without melting. When rapidly heated, vapours of tungsten hexafluoride are given off leaving a blue oxide of tungsten behind. The salt is very soluble in water, and the addition of ammonia to a conc. soln. gives a precipitate which is soluble in excess. If the aq. soln. is evaporated in air, crystals of ammonium paratungstate are formed, and a crust adheres to the walls of the vessel. When this is recrystallized from a hot ammoniacal soln., regular octahedra of **ammonium trifluotrioxytungstate** are formed—*viz.* $(NH_4)_2WO_4.4NH_4F.WO_2F_2$, or, according to A. Werner, $(NH_4)_3[WO_3F_3]$. F. Mauro said that the crystals are isomorphous with the corresponding salt of molybdenum; and H. Baker discussed its relationship with other complex salts. The salt does not change at 100°, but at a higher temp., it loses ammonia, ammonium fluoride, and hydrogen fluoride. Water dissolves all but a small residuum; aq. ammonia dissolves the salt freely and when the soln. is evaporated ammonium paratungstate is formed.

J. C. G. de Marignac obtained crystals of **sodium tetrafluodioxytungstate,** $2NaF.WO_2F_2$, or $Na_2[WO_2F_4]$, from soln. of the normal or acid tungstates in hydrofluoric acid. J. J. Berzelius also prepared a similar salt. J. C. G. de Marignac said that the crystals are probably monoclinic; they melt at a dull red-heat. There is very little loss if the salt is heated in a closed vessel, but in air, the molten mass becomes yellow probably by the separation of tungsten trioxide, and there is a loss of 13·5 to 13·7 per cent. A soln. of potassium paratungstate in an excess of hydrofluoric acid furnishes rhombic bipyramids of **potassium trifluodioxytungstate,** $KF.WO_2F_2.H_2O$, or $K[WO_2F_3(H_2O)]$, with the axial ratios $a:b:c=0·5243:1:0·7349$, and isomorphous with the ammonium salt. The salt loses all its water at 100°; and when heated to a higher temp. it behaves like the tetrafluodioxytungstate. The salt acquires a yellow colour when heated; it is soluble in water with decomposition. The salt can be recrystallized in the presence of an excess of hydrofluoric acid, otherwise **potassium tetrafluodioxytungstate,** $2KF.WO_2F_2.H_2O$, or $K_2[WO_2F_4].H_2O$, is formed—*vide supra* for the alternative formula. This salt was prepared by J. J. Berzelius, J. C. G. de Marignac, G. Marchetti, and A. Piccini from a soln. of tungsten trioxide in hydrofluoric acid, and adding potassium hydroxide, or from a hydrofluoric acid soln. of potassium tungstate. The soln. is evaporated to dryness on a water-bath, extracted with hot water, and the filtrate cooled. The colourless plates resemble those of boric acid, or of mica; J. C. G. de Marignac observed that they are monoclinic prisms with the axial ratio $a:b:c=1·0019:1:1·0481$, and $\beta=98°\ 47'$. E. Scacchi said that the (010)-cleavage is incomplete. G. Marchetti said that the salt becomes anhydrous at 100° forming tabular crystals. J. J. Berzelius said that the salt melts at a red-heat without decomposition, and when cooled it is greenish-yellow. J. C. G. de Marignac added that if heated to redness in air, it gives off hydrogen fluoride, and forms tungsten trioxide; and ultimately normal potassium tungstate with a loss of about 16 per cent. J. J. Berzelius found that the salt is sparingly soluble in cold water, and freely soluble in hot water; and J. C. G. de Marignac observed that 100 parts of water at 15° dissolve 5·88 parts of the salt. J. J. Berzelius said that the salt can be crystallized unchanged from its soln. in water, or dil. hydrochloric acid.

J. C. G. de Marignac prepared monoclinic prismatic crystals of **copper tetrafluodioxytungstate,** $CuF_2.WO_2F_2.4H_2O$, isomorphous with $CuF_2.TiF_4.4H_2O$, and with the axial ratios $a:b:c=0·7648:1:0·5629$, and $\beta=103°\ 14'$. The salt is not altered at 100°; at a higher temp. it loses water and hydrogen fluoride, ultimately forming normal copper tungstate. The salt is freely soluble in water. If an aq. soln. of this salt be mixed with ammonium fluoride, it furnishes tetragonal crystals of **ammonium copper pentafluodioxytungstate,** $NH_4F.CuF_2.WO_2F_2.4H_2O$, with the axial ratio $a:c=1:1·0945$, and isomorphous with $NH_4F.CuF_2.TiCl_4.4H_2O$. J. C. G. de Marignac obtained **silver tetrafluodioxytungstate** as a deliquescent mass which easily decomposes; and **zinc tetrafluodioxytungstate,** $ZnF_2.WO_2F_2.10H_2O$, or $Zn[WO_2F_4].10H_2O$, in triclinic crystals which effloresce in dry air, and melt in their water of crystallization below 100°. The salt is easily soluble in water. The corresponding **cadmium tetrafluodioxytungstate** is easily decomposed, and is very deliquescent. F. Ephraim and L. Heymann prepared **thallous trifluodioxytungstate,** $TlF.WO_2F_2$, and **thallous tetrafluodioxytungstate,** $2TlF.WO_2F_2$, in rhombic plates, from a conc. hydrofluoric acid soln. of tungsten trioxide mixed with thallous fluoride in the cold; hot soln. furnish **thallous heptafluotetroxyditungstate,** $3TlF.2WO_2F_2$, in long prisms. J. C. G. de Marignac prepared **manganese tetrafluodioxytungstate** which is easily decomposed and very deliquescent; and **nickel tetrafluodioxytungstate,** $NiF_2.WO_2F_2.10H_2O$, in deliquescent crystals. A. Miolati and G. Rossi prepared **cobaltic hexamminoheptafluotetroxyditungstate,** $[Co(NH_3)_6]F_3.2WO_2F_2$, as a yellow crystalline powder, by adding the hexamminotrifluoride to a soln. of tungsten trioxide in hydrofluoric acid, and crystallizing from the soln. in dil. acid. The crystals are stable at 110°.

A. Piccini [5] prepared **potassium tetrafluotrioxypertungstate,** $2KF.WO_3F_2.H_2O$, by cooling a hot soln. of potassium tetrafluodioxytungstate in hydrogen dioxide, washing the product with water, and recrystallizing from hydrofluoric acid mixed with hydrogen dioxide. The tabular crystals are not changed in air; they give off water vapour at 100°; at 150°, oxygen comes off; and after a prolonged heating in air, normal potassium tungstate remains. The salt is sparingly soluble in cold water, and freely soluble in hot water. The aq. soln. is fairly stable. According to A. Mazzucchelli and C. Barbero, the oxidation potential of a soln. of a mol of the salt in 15 litres of water is 0·787 to 0·751 volt.

REFERENCES.

[1] J. J. Berzelius, *Ann. Phil.*, **3**. 245, 1814; *Schweigger's Journ.*, **16**. 476, 1816; *Pogg. Ann.*, **4**. 147, 1825; **8**. 267, 1826; *Ann. Chim. Phys.*, (2), **17**. 13, 1821; A. Riche, *Recherches sur le tungstène et ses composés*, Paris, 1857; *Ann. Chim. Phys.*, (3), **50**. 5, 1856; H. Moissan, *ib.*, (7), **8**. 570, 1896; *Compt: Rend.*, **123**. 13, 1896.

[2] A. Rosenheim and T. H. Li, *Ber.*, **56**. B, 2228, 1923.

[3] O. Ruff and F. Eisner, *Ber.*, **38**. 742, 1905; O. Ruff, F. Eisner and W. Heller, *Zeit. anorg. Chem.*, **52**. 256, 1907.

[4] J. C. G. de Marignac, *Ann. Chim. Phys.*, (3), **69**. 5, 1862; (4), **3**. 5, 1864; *Arch. Sciences Genève*, (2), **23**. 167, 249, 1865; *Compt. Rend.*, **55**. 888, 1862; **58**. 809, 1864; J. J. Berzelius, *Ann. Phil.*, **3**. 245, 1814; *Schweigger's Journ.*, **16**. 476, 1816; *Pogg. Ann.*, **4**. 147, 1825; **8**. 267, 1826; *Ann. Chim. Phys.*, (2), **17**. 13, 1821; R. D. Hall and E. F. Smith, *Proc. Amer. Phil. Soc.*, **44**. 177, 1905; *Chem. News*, **92**. 220, 232, 242, 252, 262, 276, 1905; *Journ. Amer. Chem. Soc.*, **27**. 1384, 1905; R. D. Hall, *ib.*, **26**. 1238, 1904; *Observations on the Metallic Acids*, Easton, Pa., 1904; F. Mauro, *Atti Accad. Lincei*, (4), **4**. 481, 1888; (4), **4**. 249, 1889; (4), **5**. 398, 1889; *Gazz. Chim. Ital.*, **18**. 120, 1888; **19**. 179, 1889; E. Scacchi, *Atti Accad. Lincei*, (4), **2**. 331, 1886; (5), **2**. ii, 401, 1893; A. Miolati and G. Rossi, *ib.*, (5), **5**. ii, 183, 233, 1896; H. Baker, *Journ. Chem. Soc.*, **35**. 769, 1879; A. Werner, *Zeit. anorg. Chem.*, **9**. 386, 1895; A. Piccini, *ib.*, **2**. 21, 1892; **10**. 438, 1895; G. Marchetti, *ib.*, **10**. 66, 1895; J. W. Mallet, *Amer. Chem. Journ.*, **3**. 189, 1881; *Chem. News*, **44**. 164, 1881; F. Ephraim and L. Heymann, *Ber.*, **42**. 4456, 1909.

[5] A. Piccini, *Zeit. anorg. Chem.*, **2**. 21, 1892; A. Mazzucchelli and C. Barbero, *Atti Accad. Lincei*, (5), **15**. ii, 35, 109, 1906.

§ 19. The Tungsten Chlorides

H. E. Roscoe [1] reported **tungstous chloride,** or **tungsten dichloride,** WCl_2, to be formed by heating in a bath of molten zinc tungsten tetrachloride in a current of carbon dioxide; or by tungsten hexachloride in hydrogen. H. E. Roscoe described the product as a grey, amorphous mass, which is not stable in air. When heated in hydrogen previously passed over warm nitric acid, it forms ammonium nitrite. Water dissolves a little of the dichloride forming a brown soln., but hydrogen is slowly evolved and a brown oxide and hydrochloric acid are produced. W. Hampe said that the dichloride is infusible.

J. B. Hill found that it is difficult to control the reduction of the hexachloride by sodium amalgam, or potassium-sodium alloy, and the yield of dichloride is poor. According to K. Lindner and co-workers, tungsten dichloride cannot be prepared from the metal and carbonyl chloride, because, over a wide range of temp., carbon and red oxytetrachloride, as well as tungsten hexachloride and pentachloride are formed. The hexachloride is readily reduced to the dichloride when it is heated with powdered quartz and aluminium, magnesium, zinc, or lead in a current of nitrogen. The product is extracted with hydrochloric acid, and the reddish-yellow extract is concentrated and saturated with hydrogen chloride, thus causing the separation of **chloroaquotungstous acid,** $H[W_3Cl_7(H_2O)].3H_2O$, in slender, yellow needles which are much less stable than the corresponding compound of molybdenum. The mol. wt. of $C_5H_5N.H[W_3Cl_7]$, calculated from the f.p. of soln. in nitrobenzene is 889, when the theoretical value is 901. K. Lindner made some observations on the constitution of the salt. Chloroaquotungstous acid readily loses hydrogen chloride when exposed to air. In alcoholic soln., or on gently heating, a mol. of hydrogen chloride is evolved, and there remains a yellow insoluble residue of *monohydrate,* $W_3Cl_6.H_2O$. The compound is soluble in alkali-lye with the evolution of hydrogen and the formation of alkali tungstate. J. B. Hill said that the aq. soln. of chloroaquotungstous acid when treated with potassium hydroxide forms a clear yellow soln., which rapidly darkens, and from which weak acids precipitate a black, gelatinous precipitate of hydrated W_2O_3. The brown alkaline soln., on keeping for twenty-four hours in the air, slowly loses its colour, and when treated with weak acids yields a yellow, gelatinous precipitate of hydrated WO_2. According to K. Lindner and A. Köhler, hydrolysis with a little water furnishes the *dihydrate,* $[W_3Cl_4(H_2O)_2]Cl_2$, whereas with an excess of water, tungstic acid is formed. Sulphuric acid converts it into $W_3Cl_4(SO_4)$; and hydrobromic acid into $H[W_3Br_4Cl_3(H_2O)].9H_2O$. J. B. Hill said that chloroaquotungstous acid is soluble in alcohol, acetone, acetic acid, and mixtures of alcohol and ether, but almost insoluble in ether. K. Lindner and A. Köhler prepared a number of complex salts with pyridine: $C_6H_5N.H[W_3Cl_7(H_2O)]$, in yellow leaflets $C_5H_5N.H[W_3O_7].3H_2O$; $(C_5H_5N)_3H_3[W_3Cl_9]$, in yellow octahedra; $C_5H_5N.H[W_3Cl_7(C_5H_5N)].2(C_2H_5)_2O$; and $C_2H_4(NH_2)_2.H_2[W_3Cl_7]_2.2H_2O$. W. Biltz and C. Fendius gave 5·436 for the sp. gr. of the anhydrous chloride at 25°/4°, and 46·9 for the mol. vol. F. W. Bergstrom found that a slightly soluble ammoniobasic halide is formed with liquid ammonia.

R. F. Bernhardi-Grisson[2] found that in the electrolytic reduction of hydrofluoric acid, or aq. alcoholic soln. of tungstic acid, the reddish-brown liquid behaves towards potassium permanganate, or an ammoniacal soln. of silver nitrate as if it contained a tervalent tungsten salt. O. Olsson also was able to reduce soln. of tungstic acid to tervalent tungsten, by means of tin, and from the soln., he prepared complex salts of **tungsten trichloride,** WCl_3. O. Collenberg and co-workers discussed the electrolytic reduction of hydrochloric acid soln. of tungstic acid to the tervalent stage—*vide supra,* tungsten trioxide; and K. Someya, the titration of soln. of tungsten trichloride with copper sulphate soln. A soln. of tungstic acid in conc. hydrochloric acid was prepared by gradually adding a soln. of potassium metatungstate to boiling hydrochloric acid. The soln. at 40° to 60° is then reduced with tin until the colour is a deep green; it is then rapidly filtered through glass wool, and the filtrate sat. with hydrogen chloride, cooling meanwhile with a freezing mixture. A yellowish-green to yellowish-brown powder gradually separates; the current of hydrogen chloride is stopped after six to seven hours, and the crystals allowed to deposit for twenty-four hours, after which time they are collected, washed with alcohol and ether, dried in a current of carbon dioxide, and preserved in a carbon dioxide desiccator. The yield of **potassium tungsten enneachloride,** $K_3W_2Cl_9$, is about 50–55 per cent. A. Rosenheim and E. Dehn also prepared this salt. If ammonium metatungstate is employed in place of the potassium salt, **ammonium tungsten enneachloride,** $(NH_4)_3W_2Cl_9$, is formed. O. Collenberg and K. Sandved found that 100 c.c. of a soln. at 20° has 15·4 grms. of the potassium salt. O. Collenberg and K. Sandved found the f.p. of soln. with 9·362, 3·521, and 0·8681 grm. $K_3W_2Cl_9$ per 100 grms. of water are lowered respectively 0·639°, 0·267°, and 0·078°, corresponding with the respective osmotic factors $i=2·95$, 3·28, and 3·89. The eq. conductivity, λ, and the degree of ionization, a, for soln. with an eq. of the salt in v litres of water at 1°, are :

v .	8	16	32	64	128	256	∞
λ .	55·8	61·0	65·5	69·8	75·1	78·4	86·3
a .	—	0·71	0·76	0·81	0·87	0·91	—

P. Ray and H. Bhar gave $-0{\cdot}265\times10^{-6}$ mass unit for the magnetic susceptibility. O. Olsson added that by treating the potassium salt with a hydrochloric acid soln. of rubidium chloride, **rubidium tungsten enneachloride,** $Rb_3W_2Cl_9$, is formed; and similarly with **cæsium tungsten enneachloride,** $Cs_3W_2Cl_9$, and **thallous tungsten enneachloride,** $Tl_3W_2Cl_9$. All these salts are anhydrous, have the general formula $M_3W_2Cl_9$, and crystallize in thin, hexagonal plates, which have a greenish-yellow colour in transmitted light. The conc. aq. soln. are green, becoming greenish-yellow on dilution. The solubility decreases as the atomic weight of the alkali metal increases. They can be preserved for several days when dry, but are rapidly oxidized when moist. The solutions show no characteristic absorption bands, but a general absorption at either end of the spectrum, the visible spectrum extending from $\lambda=700$ to $\lambda=520$ for a soln. of 1 grm. of the potassium salt in 100 c.c. of 3 per cent. hydrochloric acid, the thickness of the absorbing layer being 1 cm. For a soln. containing 0·1 grm. of the salt per 100 c.c., the spectrum extends from $\lambda=100$ to $\lambda=490$. O. Collenberg and K. Sandved obtained a soln. of the free acid, **enneachloroditungstic acid,** $H_3W_2Cl_9$, by treating the thallous salt with hydriodic acid, but the acid itself could not be isolated. The term " ous " and " ic " lose their significance in the case of the multivalent elements like vanadium, molybdenum, etc.—*vide* **9**. 54, 6. Some such system as that suggested by A. Werner is required—*e.g.* bivalent tungsten compounds are tungst**i**-compounds ; tervalent tungsten, **tungsto ;** quadrivalent tungsten, tungst**e-** ; quinquevalent tungsten, tungst**an-** ; and sexivalent tungsten, tungst**on-**.

According to O. Collenberg and K. Sandved, the complex character of the potassium salt can be demonstrated by ionic migration ; and the lowering of the f.p. of aq. soln. indicate that not more than four ions are formed by ionization : $K_3W_2Cl_9 \rightleftharpoons 3K^{\cdot}+W_2Cl_9'''$. The salts are strong reducing agents since soln. of copper, silver, gold, and mercury are readily reduced ; and strong oxidizing agents oxidize tervalent tungsten to tungstic acid. The reaction is quantitative with ferric salts. The stability of the complex anion, W_2Cl_9''', is shown by the interaction of the potassium salt with copper, silver, and cadmium salts in the presence of conc. aq. ammonia to form ammines without the precipitation of tungsten hydroxide. These compounds are usually sparingly soluble in water ; the conc. aq. soln. are green, and they become yellow on dilution. The following salts are prepared by double decomposition as just indicated ; and the soln. are fairly stable—more so in the presence of hydrochloric acid. The solubilities are expressed in grams of salt per 100 c.c. of soln. at 20°. **Potassium copper tungsten tetramminoenneachloride,** $KCu(NH_3)_4W_2Cl_9.H_2O$, is a crystalline powder with a solubility of 1·85 grms. ; **ammonium copper tungsten tetramminoenneachloride,** $NH_4Cu(NH_3)_4W_2Cl_9.H_2O$, is a green crystalline powder with a solubility of 2·17 grms. ; silver tungsten hexamminoenneachloride, $[Ag(NH_3)_2]_3W_2Cl_9$, is unstable towards air and water, losing ammonia, and depositing silver ; **potassium cadmium tungsten tetramminoenneachloride,** $KCd(NH_3)_4W_2Cl_9$, has a solubility of 1·9 grms. ; **ammonium cadmium tungsten tetramminoenneachloride,** $NH_4Cd(NH_3)_4W_2Cl_9$, has a solubility of 2·17 grms. ; **chromium tungsten hexamminoenneachloride,** $Cr(NH_3)_6W_2Cl_9.2H_2O$, forms dark green, microscopic, rectangular prisms ; and **cobalt tungsten hexamminoenneachloride,** $Co(NH_3)_6W_2Cl_9.6H_2O$, is a bright green, microcrystalline powder of solubility 0·96 grms. In addition, salts of pyridine, hexamethylenetetramine, tetramethylammonium, tetraethylammonium, triethylamine, dimethylamine, aniline, phenyltrimethylammonium, p-tolyltrimethylammonium, and trimethylsulphine have been described.

A. Riche[3] prepared impure **tungsten tetrachloride,** WCl_4, in voluminous, greyish-brown crystals, by the partial reduction of the hexachloride, a reaction studied by F. Wöhler, and J. B. von Borck. A. Michael and A. Murphy obtained the tetrachloride by heating tungsten dioxide for many hours at 250° in a sealed tube with carbon tetrachloride. According to H. E. Roscoe, the tetrachloride is formed by distilling in a current of hydrogen or carbon dioxide a mixture of the pentachloride and hexachloride heated by a sulphuric acid bath; the non-volatile portion is mixed with the volatile portion, and the distillation repeated to convert any dichloride to tetrachloride. The non-volatile portion obtained in the preparation of the pentachloride is mainly the tetrachloride. The flocculent, hygroscopic, greyish-brown, crystalline mass neither fuses nor volatilizes when strongly heated, but at a high temp. it decomposes into the volatile pentachloride, and the non-volatile dichloride. W. Hampe also found it to be infusible. W. Biltz and C. Fendius gave 4·624 for the sp. gr. of the anhydrous chloride, and 70·5 for the mol. vol. H. E. Roscoe added that hydrogen at the temp. of a zinc-bath reduces the tetrachloride to metal. The salt is hydrolyzed by water forming a brown oxide and a greenish-brown hydrochloric acid soln. which deposits the brown oxide on standing some time. O. C. M. Davis found that it unites with nitrogen tetrasulphide to form **tungsten nitrogen tetrachlorotetrasulphide,** $WCl_4.N_4S_4$, in brown crystals which readily decompose. A. W. Cronander reported the complex $WCl_4.PCl_5$ to be formed when tungsten hexachloride is heated with phosphorus pentachloride. There appears to be something wrong with this statement. According to O. Olsson, when the soln. obtained by gradually adding potassium tungstate to boiling hydrochloric acid is reduced with tin at the ordinary temp., it first becomes light blue in colour, the colour then gradually deepens, and finally suddenly changes to an intense reddish-violet colour, similar to that of permanganate. This colour persists for a long time, and a small quantity of a dark green powder deposits, consisting of quadratic, tabular crystals of **potassium tungsten hydroxypentachloride,** $K_2W(OH)Cl_5$. They are red in transmitted light. The salt is stable when dry, but oxidizes rapidly when moist. The absorption spectrum of the hydrochloric acid soln. is similar to that of the tervalent compounds, the visible spectrum for a soln. of 1 grm. in 150 c.c. of 4 per cent. hydrochloric acid and a thickness of 1 cm. extending from $\lambda=730$ to $\lambda=610$.

C. W. Blomstrand[4] showed that **tungsten pentachloride,** WCl_5, reported by F. J. Malaguti, was probably the oxytetrachloride; and the pentachloride of J. B. von Borck, and V. Forcher, a mixture of the hexachloride and oxytetrachloride. C. W. Blomstrand prepared the pentachloride by heating the hexachloride for a long time in hydrogen, so as to avoid volatilization; the substance gradually becomes less fusible, and shows no inclination to crystallize on cooling. If the temperature is too high, some tungsten, or, according to H. E. Roscoe, tungsten dichloride may be formed. C. W. Blomstrand said that an alcohol-lamp suffices for the heating. The product is finally distilled in a current of carbon dioxide; the residue is the tetrachloride. C. W. Blomstrand added that only traces of pentachloride are formed in the distillation of the hexachloride in hydrogen, but, according to H. E. Roscoe, a reduction always occurs. If the temp. be kept but little above the b.p. of the hexachloride, the dark red colour of the vapour is seen to vanish, and a light yellow-coloured vapour makes its appearance, which soon condenses into black drops or long, shining, black needles. After two or three distillations in hydrogen a pure product is obtained. C. W. Blomstrand found only traces are formed by V. Forcher's process in which a mixture of tungsten trioxide and carbon is heated first in carbon dioxide and afterwards at a red-heat in chlorine. C. H. Ehrenfeld obtained the pentachloride along with the hexachloride and tungsten oxytetrachloride by heating a mixture of tungsten trioxide and phosphorus pentachloride. F. de Carli heated ferrotungsten at 400° to 500° in chlorine gas. The compound was prepared and analyzed by C. W. Blomstrand, H. E. Roscoe, and C. G. de Laval. R. F. Bernhardi-Grisson observed that quinquevalent tungsten can be obtained by the electrolytic reduction of a soln. of tungsten trioxide in hydrochloric acid and mixed with alcohol. O. Collenberg and co-workers studied the electrolytic reduction of hydrochloric acid soln. of tungsten trioxide to the quinquevalent state—*vide supra*, tungstic acid. Tungsten pentachloride crystallizes in long, black, shining needles, but if condensed in fine powder its colour is dark green, and the powdered crystals are also dark green like potassium manganate. W. Biltz and C. Fendius found 3·875 for the sp. gr. at 25°/4°, and 93·3 for the mol. vol. C. W. Blomstrand gave 244° for the m.p., and H. E. Roscoe said that it melts at 248° and freezes to a crystalline mass at 242°; and it boils at 275·6°. It is less readily volatilized than the hexachloride, and, according to C. W. Blomstrand, it yields a greenish-yellow vapour. H. E. Roscoe found the vapour density at 440° is 12·83 to 12·89; and at 350°, 12·14 to 12·43, in agreement with the formula WCl_5. W. Hampe said that the molten pentachloride is a non-conductor of electricity; A. Voigt and W. Biltz gave for the sp. conductivity $0{\cdot}67\times10^{-6}$ mho at 250°; $1{\cdot}35\times10^{-6}$ mho at 275°; and $1{\cdot}84\times10^{-6}$ mho at 300°. H. E. Roscoe, and C. W. Blomstrand found that the salt does not decrepitate like the hexachloride when heated; it is reduced when heated in hydrogen. In oxygen, the pentachloride rapidly forms brown vapours of the oxytetrachloride; it deliquesces in moist air, and is so hygroscopic that in air, the crystals immediately acquire a dark yellowish-green film, and small particles are converted into drops. When treated with water, there is a hissing noise, and the development of much heat, and the formation of a bluish-black oxide, and an olive-green soln. which slowly deposits a greenish oxide in the cold, rapidly when heated. B. Kalischer observed that the pentachloride unites with sulphur monochloride, brown needles are produced. According to H. E. Roscoe, and C. W. Blomstrand, boiling nitric acid forms tungsten trioxide; aq. ammonia added to the boiling aq. soln. gives a precipitate. A. W. Cronander found that tungsten and phosphorus pentachlorides react to form **tungsten phosphoenneachloride,** $WCl_4.PCl_5$—*vide* **8.** 50, 32. Alkali-lye acts more vigorously than water; likewise hydrochloric acid. B. Kalischer said that carbon disulphide dissolves very little pentachloride, but it acquires a deep blue colour; carbon tetrachloride forms a brown soln. Most organic compounds act vigorously on the pentachloride—*e.g.* methyl, ethyl, propyl, and amyl alcohols form yellow soln. with a hissing noise; the heat of the reaction may be so great that vapour is developed—*e.g.* with cinnamic aldehyde; and in some cases crystals may be formed—*e.g.* with alcohol, ether, benzaldehyde, and cinnamic aldehyde. Pyridine and quinoline do not form crystalline compounds. F. W. Bergstrom observed the pentachloride forms a red soln. of an ammoniobasic halide when it is treated with liquid ammonia. R. F. Bernardi-Grisson said that all salts of quinquevalent tungsten react according to $W^{V}+Ag^{\cdot}\rightarrow W^{IV}+Ag$ when treated with an ammoniacal soln. of a silver salt. A. Fischer and co-workers obtained a complex, $WCl_2(OC_2H_5)_3$, with quinquevalent tungsten by the electrolytic reduction of an alcoholic soln. of tungsten hexachloride.

A. Riche,[5] F. Wöhler, H. Rose, C. W. Blomstrand, C. G. de Laval, and H. E. Roscoe prepared **tungsten hexachloride,** WCl_6, by the action of chlorine on heated tungsten. The first action of ordinary dry chlorine is to form a yellow and then a red oxychloride, and afterwards the hexachloride. The red oxychloride cannot be separated by distillation from the hexachloride owing to the slight differences in their b.p. Metallic tungsten takes fire when moderately heated in chlorine. To prepare the hexachloride, the metal is first heated in a current of dry hydrogen in a tube, so as to remove completely every trace of air and moisture. The hydrogen is then replaced by dry chlorine free from air. The metal is then heated to dull redness—E. F. Smith and F. F. Exner recommended a temp. of 350°. A granular sublimate of dark violet crystals of the hexachloride is formed. When the hexachloride is prepared in quantity, the hexachloride collects as a reddish-black liquid. For purification, this liquid is distilled several times in an excess of chlorine, and finally rectified in a stream of hydrogen. F. de Carli passed chlorine over ferrotungsten at 400° to 500°, and extracted the chloride with carbon disulphide. After filtration and evaporation of the solvent, the residual chloride is purified by sublimation. E. F. Smith and F. Fleck obtained the hexachloride by heating the metal in the vapour of sulphur monochloride and an excess of chlorine—without the chlorine, the hexachloride is not formed; E. Defacqz heated tungsten disulphide in dry chlorine at a dull red-heat, and purified the product by sublimation; and A. Michael and A. Murphy heated a soln. of chlorine in carbon tetrachloride and tungsten trioxide in a sealed tube—the oxytetrachloride is produced at 240°, and the hexachloride at 280°—carbon tetrachloride alone converts the trioxide into the hexachloride at 280°. According to N. Teclu, when a mixture of a mol of tungsten trioxide and 3 mols of phosphorus pentachloride is heated in a sealed tube up to 170° to 200°, and the phosphoryl chloride removed by distillation, and finally by heating to 120° in a current of carbon dioxide, tungsten hexachloride of a high degree of purity is formed. C. H. Ehrenfeld observed that when tungsten trioxide is heated with an eq. weight of phosphorus pentachloride in an atm. of carbon dioxide, phosphoryl chloride is evolved, and a mixture of tungsten pentachloride and hexachloride is formed. The product is red-brown, melts to a dark red liquid, and gives off reddish-brown vapours resembling bromine; these condense to steel-blue isomeric forms of the hexachloride mixed with reddish-brown needles of the pentachloride. The intensity of the heat applied, and the duration of the action determine the quantity of the brown material produced. The hexachloride of course is converted into pentachloride by ignition in carbon dioxide or hydrogen. The bright red product is the oxytetrachloride. Nitrogen can be used instead of carbon dioxide but the results are not so good. According to H. Schiff, if a soln. of phosphorus pentachloride in carbon disulphide be heated with an equimolar proportion of tungsten trioxide for many days at 80° to 90° in a sealed tube, and the solvent removed by heating the product in a current of carbon dioxide, a mixture of tungsten oxychlorides, hexachloride, and lower chlorides is formed. H. Schiff also observed that when equimolar proportions of tungsten oxytetrachloride and phosphorus pentachloride are heated to 170° in a sealed tube, tungsten hexachloride is formed.

The salt was analyzed by A. Riche, C. W. Blomstrand, N. Teclu, V. Forcher, H. E. Roscoe, C. G. de Laval, A. Michael and A. Murphy, etc. The results agree with the formula WCl_6. N. V. Sidgwick discussed the co-valency of tungsten in the hexachloride. H. E. Roscoe said that the dark violet crystals of the sublimate decrepitate on cooling and the mass falls to a crystalline powder. H. E. Roscoe found that on several occasions sealed tubes exploded when opening them with a file owing to sudden decrepitation. V. Forcher described the crystals as dark violet needles or scales; and C. W. Blomstrand said that the colour in the molten state is brownish-black, with no tinge of red. The molten salt solidifies to a mass of scaly crystals. The soln. in carbon disulphide furnishes hexagonal plates. C. H. Ehrenfeld said that the crystals are steel-blue and cubic. F. Wöhler said that the vapour is the colour of nitrogen trioxide; C. W. Blomstrand said reddish-yellow; V. Forcher, dark red; and H. E. Roscoe, reddish-brown. E. F. Smith and F. F. Exner gave 3·518 for the sp. gr.; W. Biltz and C. Fendius gave 3·520 at 25°/4°, and for the mol. vol., 112·7. H. E. Roscoe found the vapour density at 440° to be 18·67, and at 350°, 13·16 in agreement with the formula WCl_6. and with the assumption that with higher temp. the molecules dissociate, rather than to assume with J. Persoz that the salt has the formula WCl_5. H. Debray, and R. Rieth also observed the anomalous vapour density at the higher temp. A. Riche, C. W. Blomstrand, and V. Forcher found that the salt softens when heated to 170° to 183°—N. Teclu said 189°—presumably owing to impurities—say oxychloride—because H. E. Roscoe found that the salt melts to a black liquid at 275°, and freezes at 270° owing to surfusion. H. Debray gave 300° for the b.p., and H. E. Roscoe, 346·7° at 759·5 mm. H. G. Grimm, and G. von Hevesy discussed the m.p. and electrical conductivity. W. Hampe found that the molten hexachloride is a non-conductor of electricity; A. Voigt and W. Biltz gave for the sp. conductivity $1{\cdot}98\times10^{-6}$ mho at 280°; $2{\cdot}85\times10^{-6}$ mho at 305°; and $6{\cdot}94\times10^{-6}$ at 330°; and W. Biltz gave 0·0000020 for the temp. coeff. of the conductivity. O. Collenberg and A. Guthe found that the reduction potential of sexivalent to quinquevalent tungsten for soln. with 0·143 gram-atom of tungsten per litre in $2N$-H_2SO_4 at 18° is 0·395 volt. S. Berkman and H. Zocher gave $-0{\cdot}14\times10^{-6}$ mass unit for the magnetic susceptibility.

The reducing action of hydrogen—*vide supra*, tungsten tetrachloride and pentachloride—was observed by A. Riche, H. E. Roscoe, W. Spring, and F. Wöhler. V. Forcher, and H. Debray said that the salt changes slowly in moist air, but H. E. Roscoe added that the purified hexachloride does not undergo any change even in moist air, but if the smallest trace of oxychloride is present, it at once absorbs moisture evolving fumes of hydrogen chloride, and changing its colour from violet to brown. V. Forcher found that, when the hexachloride is heated in air, it forms tungsten oxytetrachloride. N. Teclu, and C. W. Blomstrand said that the hexachloride is very slowly attacked by cold water, but H. E. Roscoe added that if the salt is impure, it is at once decomposed by cold water forming a greenish hydrated oxide. Water begins to attack the purified hexachloride at about 60°; boiling water decomposes it rapidly. The tungstic acid which is formed retains chlorine very tenaciously. According to C. W. Blomstrand, alkali-lye acts on the hexachloride slowly in the cold, and when heated the action is very vigorous, the salt swells up and the liquid becomes blue, and after a short time, colourless. Brown flecks separate out. If lower chlorides are present, added H. Debray, some hydrogen may be developed by the action of the alkali-lye. W. Biltz and E. Meinecke said that the hexachloride is very sparingly soluble in liquid chlorine. C. W. Blomstrand observed that hydrochloric acid produces no change at first, and when heated, the liquid remains colourless, but after a short time tungstic acid is formed; E. Defacqz found that hydrogen bromide at about 300° forms tungsten pentabromide; when heated with liquid hydrogen bromide in a sealed tube, a chlorobromide is formed whose composition depends on the temp.; hydrogen iodide forms tungsten diiodide; liquid hydrogen iodide heated in a sealed tube, forms tungsten tetraiodide; hydrogen sulphide forms tungsten disulphide; and liquid hydrogen sulphide, in a sealed tube, forms a chlorosulphide. S. Rideal found that ammonia acts rapidly on the hexachloride forming tungsten hemitrinitride; and O. C. M. Davis found that a soln. of the hexachloride soln. forms $WCl_4.N_4S_4$, as indicated above. N. Teclu said that the salt is soluble in phosphoryl chloride. A. W. Cronander studied the action of phosphorus pentachloride—*vide supra*, tungsten tetrachloride. E. Defacqz found that phosphine forms tungsten diphosphide; and arsine, tungsten diarsenide—liquid arsine in a sealed tube forms a chloroarsenide. A. Fischer and A. Roderburg found that at 18°, a red soln. of 0·2364 grm. of the hexachloride in 20 c.c. of arsenic trichloride with a sp. conductivity of $6{\cdot}2\times10^{-6}$ mho has a conductivity of $1{\cdot}3\times10^{-6}$ mho. J. N. Pring and W. Fielding observed that tungsten hexachloride is reduced by carbon at 1000°–1500°. H. E. Roscoe found that the hexachloride dissolves in carbon disulphide forming a reddish-brown soln.; O. C. M. Davis found that it is soluble in chloroform. A. Riche said that alcohol acts vigorously without forming a tungstic ether; and B. Kalischer found that the hexachloride dissolves in alcohol. The soln. is yellow, but no addition product is formed. A. Fischer and A. Roderburg found that the yellow soln. of 0·1937 grm. of the hexachloride in 20 c.c. of methyl alcohol of sp. conductivity $1{\cdot}8\times10^{-6}$ mho at 18° has a conductivity of $5{\cdot}23\times10^{-3}$ mho; and the yellow soln. of 0·4428 grm. of hexachloride in 20 c.c. of 99·8 per cent. ethyl alcohol of sp. conductivity 2×10^{-6} mho at 18°, has a conductivity of $3{\cdot}46\times10^{-3}$ mho at 18°. The eq. conductivity, λ, of an eq. of the salt in v litres of alcohol of sp. conductivity $1{\cdot}56\times10^{-6}$ mho at 2°, is:

v .	1·30	2·82	5·82	9·84	123	417	925
λ .	7·0	8·7	10·4	11·6	16·7	20·9	24·6 mho.

The e.m.f. of the cell W | WCl_6(alcohol) | LiCl(sat. soln. in alcohol) | Hg_2Cl_2 | Hg for one-sixth of a mol of the hexachloride in *v* litres is :

v	1·30	2·82	5·82	9·84	123	417	925
E.m.f.	0·504	0·492	0·474	0·465	0·399	0·362	0·349 volt.

The electrolysis of an alcoholic soln. of the hexachloride colours the liquid green as the tungsten is reduced to the quinquevalent form, and the complex $WCl_2(OC_2H_5)_3$ separates out. In opposition to the patent of the Wolframlampen A.G., no evidence of the separation of tungsten was observed with soln. in methyl alcohol, ethyl alcohol, acetone or pyridine, although with glycerol soln. a little tungsten was deposited. F. W. Bergstrom observed that the hexachloride forms a red soln. with liquid ammonia. A. Rosenheim observed that a compound with oxalic acid is formed in chloroform soln. B. Kalischer observed the formation of no addition products with aldehydes, ketones, or esters, although salicylic ether forms $WCl_4(OC_6H_4.COOC_2H_5)_2$; salicylic acid formed a similar compound. No complex salts were formed with organic chlorides in alcoholic soln. The soln. of the hexachloride in ether is yellow ; in benzene, brown ; and in chloroform, carbon disulphide, carbon tetrachloride, and ligroïn, brown or reddish-brown. The soln. gradually change owing to the reduction of the hexachloride. The change is rapid if water be present.

A. Fischer and A. Roderburg found that with a soln. of the bracketed number of grams of the hexachloride in 20 c.c. of solvent, at 18°, the colour is red with chloroform (0·203) and the sp. conductivity is $8·6\times10^{-6}$ mho when that of the pure solvent is zero ; is violet with carbon disulphide (0·2316) and the sp. conductivity of solvent and soln. is zero ; red with carbon tetrachloride (0·1899), conductivity of solvent and soln. zero ; dark blue with benzene (0·1622), sp. conductivity of solvent and soln. zero ; red with acetylene tetrachloride (0·1262), sp. conductivity of solvent zero, of soln., 9×10^{-6} mho ; dark blue with chlorobenzene (0·2201), sp. conductivity of solvent and soln. zero ; red with ethyl ether (0·2309), sp. conductivity of solvent zero, of soln., $1·5\times10^{-7}$ mho ; red with ligroïn (0·1434), sp. conductivity of solvent and soln. zero ; red with pyridine (0·1587), sp. conductivity of soln. $1·4\times10^{-7}$ mho, and of soln. $5·8\times10^{-4}$ mho ; brownish-yellow with glycerol (1·2557), sp. conductivity of solvent zero, and of soln. at 100°, $1·47\times10^{-2}$ mho ; and yellow with dried acetone (1·3443), sp. conductivity of solvent $2·4\times10^{-6}$ mho, and of soln. 2×10^{-3} mho. W. Brydowna found that tungsten hexachloride reacts with a soln. of phenyl-magnesium iodide in ether producing diphenyl.

A. Riche observed that sodium reduces the vapour of the hexachloride to tungsten ; and K. Seubert and A. Schmidt that magnesium at a red-heat reduces the hexachloride to metal. C. W. Blomstrand found that the hexachloride is reduced to a lower chloride by copper, silver, and molybdenum, but not by tungsten. H. Debray observed that when the hexachloride is heated with tungsten trioxide, the oxytetrachloride is formed.

REFERENCES.

[1] H. E. Roscoe, *Liebig's Ann.*, **162**. 359, 1872 ; *Proc. Manchester Lit. Phil. Soc.*, **11**. 79, 1872 ; *Bull. Soc. Chim.*, (2), **25**. 61, 1873 ; *Chem. News*, **25**. 61, 73, 90, 1873 ; J. B. Hill, *ib.*, **116**. 237, 1917 ; *Journ. Amer. Chem. Soc.*, **38**. 2383, 1916 ; F. W. Bergstrom, *ib.*, **47**. 2317, 1925 ; K. Lindner, *Ber.*, **55**. B, 1458, 1922 ; *Zeit. anorg. Chem.*, **160**. 57, 1927 ; **162**. 203, 1927 ; K. Lindner and A. Köhler, *ib.*, **140**. 357, 1924 ; W. Biltz and C. Fendius, *ib.*, **172**. 385, 1928 ; C. Fendius, *Zur Volumchemie und Verwandtschaftslehre der Uran-, Wolfram-, und Molybdänchloride*, Leipzig, 1928 ; W. Hampe, *Chem. Ztg.*, **12**. 106, 1888.

[2] W. Biltz and C. Fendius, *Zeit. anorg. Chem.*, **172**. 385, 1928 ; W. Biltz, *ib.*, **193**. 321, 1930 ; K. Someya, *ib.*, **162**. 207, 1927 ; R. F. Bernhardi-Grisson, *Die kathodische Reduktion der Wolframsäure*, Berlin, 1910 ; E. Dehn, *Die Cyanide des Wolframs*, Berlin, 1915 ; A. Rosenheim and E. Dehn, *Ber.*, **48**. 1167, 1915 ; O. Collenberg, *ib.*, **46**. 566, 1913 ; *Zeit. anorg. Chem.*, **88**. 49, 1914 ; O. Collenberg and K. Sandved, *ib.*, **130**. 1, 1923 ; O. Collenberg and A. Guthe, *ib.*, **134**. 317, 1924 ; O. Collenberg and J. Backer, *Zeit. Elektrochem.*, **30**. 230, 1924 ; O. Collenberg and K. Wilson, *ib.*, **31**. 555, 1925 ; P. Ray and H. Bhar, *Journ. Indian Chem. Soc.*, **5**. 497, 1928 ; A. Werner, *Neuere Anschauungen auf dem Gebiete der anorganischer Chemie*, Braunschweig, 12, 1905 ; London, 71, 1911 ; O. Olssen, *Ber.*, **46**. 566, 1913.

[3] A. Riche, *Recherches sur le tungstène et ses composés*, Paris, 1857 ; *Ann. Chim. Phys.*, (3), **50**. 5, 1856 ; F. Wöhler, *ib.*, (2), **29**. 43, 1823 ; *Quart. Journ. Science*, **20**. 177, 1826 ; *Phil. Mag.*, **66**. 263, 1825 ; *Pogg. Ann.*, **2**. 345, 1924 ; J. B. von Borck, *Oefvers. Akad. Förh.*, **8**. 149, 1851 ; *Journ. prakt. Chem.*, (1), **54**. 254, 1851 ; H. E. Roscoe, *Liebig's Ann.*, **162**. 359, 1872 ; *Proc.*

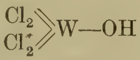
Manchester Lit. Phil. Soc., **11**. 79, 1872 ; *Bull. Soc. Chim.*, (2), **25**. 61, 1873 ; *Chem. News*, **25**. 61, 73, 90, 1873 ; A. W. Cronander, *Ber.*, **6**. 1466, 1873 ; O. C. M. Davis, *Journ. Chem. Soc.*, **89**. 1575, 1906 ; W. Biltz and C. Fendius, *Zeit. anorg. Chem.*, **172**. 385, 1928 ; C. Fendius, *Zur Volumchemie und Verwandtschaftslehre der Uran-, Wolfram-, and Molybdänchloride*, Leipzig, 1928 ; O. Olsson, *Ber.*, **46**. 566, 1913 ; A. Michael and A. Murphy, *Amer. Chem. Journ.*, **44**. 382, 1910 ; W. Hampe, *Chem. Ztg.*, **12**. 106, 1888.

[4] C. W. Blomstrand, *Journ. prakt. Chem.*, (1), **82**. 421, 1861 ; (1), **89**. 238, 1863 ; V. Forcher, *ib.*, (1), **86**. 227, 1862 ; *Bull. Soc. Chim.*, (2), **5**. 197, 1863 ; *Sitzber. Akad. Wien*, **44**. 165, 1861 ; F. J. Malaguti, *Ann. Chim. Phys.*, (2), **60**. 271, 1835 ; A. Voigt and W. Biltz, *Zeit. anorg. Chem.*, **133**. 277, 1924 ; W. Biltz, *ib.*, **193**. 321, 1930 ; W. Biltz and C. Fendius, *ib.*, **172**. 385, 1928 ; C. Fendius, *Zur Volumchemie und Verwandtschaftslehre der Uran-, Wolfram-, und Molybdänchloride*, Leipzig, 1928 ; H. E. Roscoe, *Liebig's Ann.*, **162**. 359, 1872 ; *Proc. Manchester Lit. Phil. Soc.*, **11**. 79, 1872 ; *Bull. Soc. Chim.*, (2), **25**. 61, 1873 ; *Chem. News*, **25**. 61, 73, 90, 1873 ; J. B. von Borck, *Oefvers Akad. Förh.*, **8**. 149, 1851 ; *Journ. prakt. Chem.*, (1), **54**. 254, 1851 ; R. F. Bernhardi-Grisson, *Die kathodische Reduktion der Wolframsäure*, Berlin, 1910 ; A. W. Cronander, *Bull. Soc. Chim.*, (2), **19**. 499, 1873 ; *Ber.*, **6**. 466, 1873 ; *Oefvers. Akad. Stockholm*, **27**. 57, 1870 ; C. H. Ehrenfeld, *Journ. Amer. Chem. Soc.*, **17**. 381, 1895 ; W. Hampe, *Chem. Ztg.*, **12**. 106, 1888 ; A. Roderburg, *Das elektrochemische Verhalten des Wolframs*, Aachen, 1912 ; A. Fischer and A. Roderburg, *Zeit. anorg. Chem.*, **81**. 170, 1913 ; A. Fischer and L. Michaels, *ib.*, **81**. 102, 1913 ; O. Collenberg and A. Guthe, *ib.*, **134**. 317, 1924 ; **136**. 252, 1924 ; O. Collenberg and K. Wilson, *Zeit. Elektrochem.*, **31**. 555, 1925 ; O. Collenberg and J. Backer, *ib.*, **30**. 230, 1924 ; B. Kalischer, *Zur Kenntnis der Halogenide des höherwertigen Wolframs und Molybdäns*, Berlin, 1902 ; C. G. de Laval, *Ber.*, **6**. 1464, 1873 ; *Om Wolfram*, Upsala, 1872 ; F. W. Bergstrom, *Journ. Amer. Chem. Soc.*, **47**. 2317, 1925 ; F. de Carli, *Atti Congr. Chim. Pure Appl.*, 399, 1923.

[5] C. G. de Laval, *Ber.*, **6**. 1464, 1873 ; *Om Wolfram*, Upsala, 1872 ; A. Riche, *Recherches sur le tungstène et ses composés*, Paris, 1857 ; *Ann. Chim. Phys.*, (3), **50**. 5, 1856 ; H. E. Roscoe, *Liebig's Ann.*, **162**. 359, 1872 ; *Proc. Manchester Lit. Phil. Soc.*, **11**. 79, 1872 ; *Bull. Soc. Chim*, (2), **25**. 61, 1873 ; *Chem. News*, **25**. 61, 73, 90, 1873 ; C. W. Blomstrand, *Journ. prakt. Chem.*, (1), **82**. 421, 1861 ; (1), **89**. 238, 1863 ; V. Forcher, *ib.*, (1), **86**. 227, 1862 ; *Bull. Soc. Chim.*, (2), **5**. 197, 1863 ; *Sitzber. Akad. Wien*, **44**. 165, 1861 ; C. H. Ehrenfeld, *Journ. Amer. Chem. Soc.*, **17**. 381, 1895 ; B. Kalischer, *Zur Kenntnis der Halogenide des höherwertigen Wolframs und Molybdäns*, Berlin, 1902 ; E. F. Smith and F. Fleck, *Journ. Amer. Chem. Soc.*, **21**. 1007, 1899 ; J. B. Hill, *Chem. News*, **116**. 237, 1917 ; *Journ. Amer. Chem. Soc.*, **38**. 2383, 1916 ; E. F. Smith and F. F. Exner, *ib.*, **26**. 1082, 1904 ; *Chem. News*, **90**. 66, 1904 ; E. Defacqz, *Compt. Rend.*, **128**. 610, 1232, 1899 ; **129**. 515, 1899 ; *Ann. Chim. Phys.*, (7), **22**. 244, 1901 ; *Contribution à l'étude du tungstène et de ses composés*, Paris, 1901 ; H. Schiff, *Liebig's Ann.*, **197**. 188, 1879 ; K. Seubert and A. Schmidt, *ib.*, **267**. 218, 1892 ; F. Wöhler, *ib.*, **95**. 255, 1855 ; N. Teclu, *ib.*, **187**. 225, 1877 ; H. Rose, *ib.*, **40**. 395, 1837 ; H. Debray, *Compt. Rend.*, **60**. 820, 1865 ; J. Persoz, *ib.*, **58**. 1196, 1864 ; *Bull. Soc. Chim.*, (2), **2**. 188, 1864 ; *Ann. Chim. Phys.*, (4), **1**. 93, 1864 ; F. Wöhler, *ib.*, (2), **29**. 43, 1823 ; *Quart. Journ. Science*, **20**. 177, 1826 ; *Phil. Mag.*, **66**. 263 1825 ; *Pogg. Ann.*, **2**. 345, 1924 ; J. N. Pring and W. Fielding, *Journ. Chem. Soc.*, **95**. 1502, 1909 ; O. C. M. Davis, *ib.*, **89**. 1575, 1906 ; S. Rideal, *ib.*, **55**. 41, 1889 ; N. V. Sidgwick, *ib.*, **125**. 2672, 1924 ; O. Ruff, *Ber.* **34**. 3509, 1901 ; R. Rieth, *ib.*, **3**. 666, 1870 ; A. W. Cronander, *ib.*, **6**. 1466, 1873 ; Wolframlampen A.G., *German Pat., D.R.P.* 231657, 237014, 1910 ; W. Spring, *Zeit. anorg. Chem.*, **1**. 242, 1892 ; W. Biltz, *ib.*, **133**. 306, 1924 ; A. Voigt and W. Biltz, *ib.*, **133**. 277, 1924 ; W. Biltz and E. Meinecke, *ib.*, **131**. 1, 1923 ; W. Biltz, *ib.*, **193**. 321, 1930 ; W. Biltz and C. Fendius, *ib.*, **172**. 385, 1928 ; C. Fendius, *Zur Volumchemie und Verwandtschaftslehre der Uran-, Wolfram-, und Molybdänchloride*, Leipzig, 1928 ; O. Collenberg and A. Guthe, *Zeit. anorg. Chem.*, **136**. 252, 1924 ; A. Rosenheim, *ib.*, **4**. 371, 1893 ; A. Fischer and A. Roderburg, *ib.*, **81**. 170, 1913 ; A. Roderburg, *Das elektrochemische Verhalten des Wolframs*, Aachen, 1912 ; A. Michael and A. Murphy, *Amer. Chem. Journ.*, **44**. 382, 1910 ; W. Hampe, *Chem. Ztg.*, **12**. 106, 1888 ; W. Brydowna, *Bull. Soc. Chim.*, (4), **39**. 1771, 1926 ; F. W. Bergstrom, *Journ. Amer. Chem. Soc.*, **47**. 2317, 1925 ; F. de Carli, *Atti Congr. Naz. Chim. Pure Appl.*, 399, 1923 ; S. Berkman and H. Zocher, *Zeit. phys. Chem.*, **124**. 318, 1926 ; G. von Hevesy, *Zeit. Elektrochem.*, **34**. 463, 1928 ; H. G. Grimm, *ib.*, **34**. 430, 1928.

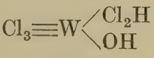
§ 20. The Tungsten Oxychlorides

O. Olsson [1] prepared **potassium tungsten hydroxylpentachloride,** $K_2W(OH)Cl_5$, as indicated in connection with tungsten tetrachloride. B. Kalischer's attempts to prepare **tungsten oxytrichloride,** $WOCl_3$, with quinquevalent tungsten were not successful, but O. O. Collenberg obtained complex salts of this oxychloride. A soln. of an alkali tungstate in a conc. soln. of oxalic acid containing a slight excess of alkali oxalate was reduced with tin. The course of the reduction can be followed by the colour change, through dark blue, green, and yellow to deep red. After removal of tin and excess of oxalic acid, the complex oxalate is precipitated by means of alcohol, and can be purified by dissolving in hot water and salting out the sodium salt with sodium bromide, and the potassium salt with potassium iodide. The compounds must be dried in a current of carbon dioxide, but are fairly stable in air when dry. The sodium salt has the composition $3Na_2O.2W_2O_5.4C_2O_3.12H_2O$, and the potassium salt $3K_2O.2W_2O_5.4C_2O_3.9H_2O$. They are red, crystalline powders which slowly oxidize in air, and at 100° lose their water, but do not decompose. They are very soluble in water, insoluble in organic solvents. These complex oxalates are supposed to be derived from a hypothetical tungstous acid, $WO_2.OH$. The oxalotungstites dissolve in concentrated hydrochloric acid, forming a deep blue soln., which contains an *oxychloride* of quinquevalent tungsten, probably $WOCl_3$. From this soln., complex chlorides can be isolated containing $WOCl_3$ in combination with chlorides of the alkali metals or ammonium or hydrochlorides of organic bases. The ammonium and potassium salts are precipitated by saturating a hydrochloric acid soln. of the corresponding oxalotungstite with hydrogen chloride. The rubidium, cæsium, aniline, tetraethyl- and tetrapropyl-ammonium compounds are precipitated when the corresponding chloride is added to a hydrochloric acid soln. of an oxalotungstite, and the pyridine and quinoline compounds are prepared by double decomposition of their hydrochlorides with ammonium chlorotungstite. There are two main types of salt, those derived from $2RCl.WOCl_3$, or R_2WOCl_5, and those derived from $RCl.WOCl_3$, or $RWOCl_4$. The co-ordination formulæ are respectively $R_2[WOCl_5]$, and $R[WOCl_4(H_2O)]$. The $RCl.WOCl_3$ compounds can be regarded as derivatives of metatungstous acid, $WO_2.OH$, and the $2RCl.WOCl_3$ compounds as derivatives of orthotungstous acid, $W(OH)_5$, in which one oxygen is replaced by two chlorine atoms, and three hydroxyl groups by three chlorine atoms, thus :



$\left.\begin{matrix}Cl_2\\Cl_2\end{matrix}\right\rangle W{-}OH$

$RCl.WOCl_3$



$Cl_3{\equiv}W\left\langle\begin{matrix}Cl_2H\\OH\end{matrix}\right.$

$2RCl.WOCl_3$

A green crystalline powder of **ammonium oxypentachlorotungstite,** $(NH_4)_2WOCl_5$, is hydrolyzed by water ; 20 c.c. of hydrochloric acid dissolve a gram of the salt ; and it is soluble in absolute methyl or ethyl alcohol. Similarly with **potassium oxypentachlorotungstite,** $K_2WOCl_5.2H_2O$, as a reddish-brown or yellowish-brown powder ; **rubidium oxypentachlorotungstite,** Rb_2WOCl_5 ; and with **cæsium oxypentachlorotungstite,** Cs_2WOCl_5. The salt with aniline was also prepared. Salts of the type $RCl.WOCl_3$, were prepared with pyridine, quinoline, tetraethylammonium, and tetrapropylammonium. These salts are stable in dry air at the ordinary temp., but decompose with oxidation to tungstates at 60° to 70°. They are immediately hydrolyzed by water with the formation of a brown hydroxide. The less soluble cæsium compound is, however, far more stable than the readily soluble ammonium and potassium compounds. The salts dissolve readily in absolute methyl and ethyl alcohols, with the exception of the rubidium and cæsium compounds, but not in other organic solvents. Conc. hydrochloric acid and 35 per cent. sulphuric acid also dissolve them, but alkalies and aq. ammonia decompose them. Oxidizing agents convert them into tungstates, and permanganate and iodine have been employed for quantitative determinations of the quinquevalent tungsten. The chlorotungstites react vigorously with a conc. soln. of potassium cyanide with evolution of hydrogen cyanide. A reddish-brown soln. is formed containing cyanides of the type $M_4W(CN)_8$. A thiocyanic acid compound has also been isolated in the form of a pyridine salt. P. Ray and co-workers found the magnetic susceptibility of $K_2W(OH)Cl_5$ to be $4{\cdot}0\times10^{-6}$ mass unit at 31°.

F. Wöhler [2] discovered **tungsten oxytetrachloride,** $WOCl_4$, which he obtained by heating the sulphide in chlorine. J. B. von Borck, F. J. Malaguti, and C. G. de Laval used a similar process. C. W. Blomstrand, and V. Forcher said that the " sulphide " was probably the oxysulphide, or air and moisture were not excluded from the system. A similar remark applies to the formation of the oxytetrachloride observed by J. B. von Borck, C. W. Blomstrand, and H. E. Roscoe when chlorine containing air and moisture is passed over heated tungsten, or, according to A. Vosmaer, ferrotungsten. This subject was also studied by J. Persoz, R. Weber, N. Teclu, H. Schiff, C. Gerhardt and L. Chiozza, and A. Kremer. H. Debray, C. W. Blomstrand, C. G. de Laval, and H. E. Roscoe considered that the oxytetrachloride is best obtained by passing the vapour of tungsten hexachloride over heated tungsten trioxide or dioxydichloride. O. Ruff and co-workers recommended the following process :

> A hard glass tube 50 cms. long was packed with tungsten hexachloride in the first third of its length, and with tungsten dioxydichloride in the middle third, while the last third was left for the reception of the oxytetrachloride. The middle part of the tube, wrapped in asbestos, was heated to about 230°, while a current of well-dried carbon dioxide is passed through the tube. When all the air has been displaced, the part containing the hexachloride is heated directly by the flame so that the hexachloride slowly boils. The current of carbon dioxide carries the vapour over the dioxydichloride, and reddish needles of the oxytetrachloride sublime into the cooler part of the tube. The product is resublimed in a current of carbon dioxide to remove traces of hexachloride and dioxydichloride.

A. Bonnet, and A. Riche obtained the salt by heating a mixture of tungsten trioxide and carbon in a current of dry carbon dioxide until all the air and moisture is expelled, and then in a current of dry chlorine. It is purified by distillation in a current of carbon dioxide. R. D. Hall, and E. F. Smith and F. Fleck prepared the oxytetrachloride by passing sulphur monochloride vapour over tungsten trioxide, or wolframite, or scheelite at 145°, and purifying the product by distillation between 215° and 225°. F. Bourion, and C. Matignon and F. Bourion passed the vapour of sulphur monochloride alone or mixed with hydrogen chloride over tungsten trioxide at 230° to 250° and cooled the product in a current of hydrogen chloride. When the vapour of sulphur monochloride is passed over wolframite or scheelite heated to about 150°, prismatic scarlet crystals are obtained when the red soln. cools. Similar crystals are obtained by the action of the same substance on tungsten trioxide. The third oxygen atom of tungsten trioxide is not removed by heating with sulphur monochloride. The product is immediately decomposed on exposure to air, it gives off hydrogen chloride and leaves tungsten trioxide. This salt is readily soluble in carbon disulphide or sulphur monochloride, but sparingly soluble in benzene. Sulphur monochloride does not attack tungsten itself. C. W. Watts and C. A. Bell, and H. E. Quantin heated tungsten trioxide in the vapour of carbon tetrachloride and obtained a mixture of the dioxydichloride and oxytetrachloride ; P. Camboulives recommended for the oxytetrachloride a temp. of 560°, and A. Michael and A. Murphy added that one of the best methods of preparing the oxytetrachloride is to heat tungsten trioxide with a soln. of chlorine in carbon tetrachloride in a sealed tube at 240°. C. W. Watts and C. A. Bell said that a mixture of chlorine and carbon monoxide, or dioxide, can be substituted for carbon tetrachloride ; and E. F. Smith and V. Oberholtzer, and K. Lindner recommended passing the vapour of carbonyl chloride over red-hot tungsten. H. Schiff observed that the oxytetrachloride is formed by heating a mol of tungsten trioxide with one or two mols of phosphorus pentachloride, and sublimation of the product in a current of carbon dioxide to separate the more volatile oxytetrachloride from the less volatile dioxydichloride. E. H. Ehrenfeld obtained a mixture of chlorides and oxychlorides by the action of phosphorus pentachloride on tungsten trioxide. G. Rauter heated the trioxide in the presence of silicon tetrachloride, although E. H. Ehrenfeld said that silicon tetrachloride does not act on tungsten trioxide. H. Rose, C. W. Blomstrand, and V. Forcher prepared the oxytetrachloride by heating the dioxydichloride in hydrogen ; C. W. Blomstrand heated tungsten pentachloride in oxygen, and C. G. de Laval, the hexachloride in oxygen ; and H. Debray distilled tungsten hexachloride with oxalic acid—some dioxydichloride is simultaneously formed.

Analyses in agreement with $WOCl_4$ were reported by A. Riche, H. Schiff, C. W. Blomstrand, C. G. de Laval, A. Bonnet, V. Forcher, H. E. Roscoe, etc. F. J. Malaguti represented it by the formula W_2Cl_5, and J. B. von Borck, by WCl_4. Various observers described the oxytetrachloride as forming red, or scarlet-red, prismatic needles, which, according to H. Debray, have a vapour density of 10·58, and, according to H. E. Roscoe, 11·92, which is approximately normal. The vapour is pale red; F. Wöhler said that it has the colour of nitrogen trioxide. The oxytetrachloride was found by A. Riche to melt at 199°, and solidify at 197·5°; C. W. Blomstrand gave 208° to 210° for the m.p., C. W. Blomstrand, 204°; and H. E. Roscoe, 210·4°—and 206·7° for the f.p. A. Riche, and C. W. Blomstrand found that it can be volatilized without melting, and H. E. Roscoe gave 227·5° for the b.p. W. Hampe observed that neither the molten salt nor the vapour is a conductor of electricity. L. von Uslar, and A. Riche observed that when heated in hydrogen it can be reduced to metal. F. Wöhler, J. B. von Borck, C. G. de Laval, V. Forcher, and H. E. Roscoe observed that, when exposed to air, the salt is very quickly hydrolyzed by moisture to hydrogen chloride and tungstic acid. C. W. Blomstrand found that it can be sublimed in oxygen without change, but it finally loses chlorine, passing into the dioxydichloride observed by A. Vosmaer. F. Wöhler, and A. Riche observed that it hisses when in contact with water, heat is evolved, and it is rapidly hydrolyzed into tungstic acid and hydrochloric acid. J. B. von Borck added that some hydrogen may be evolved, but this statement has not been confirmed; alkali-lye was found by V. Forcher to form tungstate, and presumably chloride. When the oxytetrachloride is mixed with carbon, and heated in chlorine, H. E. Roscoe observed that it is converted into tungsten hexachloride. S. Rideal found that ammonia converts it into a mass of black hemitrinitride; and when heated with phosphorus pentachloride in a sealed tube at about 170°, tungsten hexachloride and phosphoryl chloride are formed. E. W. Smith and F. Fleck said that the oxytetrachloride is soluble in carbon disulphide and sulphur monochloride, and sparingly soluble in benzene; and B. Kalischer added that it is not dissolved by the usual solvents.

F. Wöhler prepared **tungsten dioxydichloride,** WO_2Cl_2, by heating tungsten dioxide in dry chlorine. The reaction occurs with incandescence, and a dense, yellow vapour is formed, which forms a crystalline sublimate. V. Forcher used blue tungsten oxide, and C. G. de Laval warmed the dioxide. V. I. Spitzin and L. Kaschtanoff found that the dioxydichloride is formed when hydrogen chloride acts on tungsten dioxide, hemipentoxide, and trioxide, or on the tungstates. H. Rose, and E. F. Smith and O. L. Shinn employed a similar process. F. Wöhler, and F. J. Malaguti thought that the dioxydichloride is the hexachloride, but H. Rose showed that this is wrong. It was analyzed by H. Rose, A. Riche, J. B. von Borck, C. G. de Laval, H. E. Roscoe, and O. Ruff and co-workers. A. Riche obtained the dioxydichloride by heating tungsten trioxide in dry chlorine; V. Forcher similarly heated a mixture of carbon and tungsten trioxide or wolframite; and J. B. von Borck heated tungsten in a mixture of chlorine and air. F. Bourion heated tungsten trioxide in the vapour of sulphur monochloride and obtained both the dioxydichloride and the oxytetrachloride. C. W. Watts and C. A. Bell passed the vapour of carbon tetrachloride over red-hot tungsten trioxide; H. Debray heated tungsten hexachloride with oxalic acid—*vide supra*, tungsten oxytetrachloride; and C. G. de Laval sublimed tungsten hexachloride or pentachloride over the heated trioxide. H. O. Schulze heated in the absence of air a mixture of calcium chloride and tungsten trioxide, and obtained tungsten dioxydichloride and calcium tungstate—the chlorides of magnesium, iron, cobalt, and nickel can be used, but not the alkali, lead, or silver chlorides.

Tungsten dioxydichloride obtained by sublimation was described by F. Wöhler, A. Riche, C. G. de Laval, V. Forcher, and H. E. Roscoe as a pale yellow or dark golden-yellow solid with four-sided plates resembling natural boric acid; and the vapour is variously described as pale yellow, or dark red. H. Debray, and H. E. Roscoe said that complete volatilization does not occur at 450°, and no vapour density determination was made at this temp. H. Rose said that when suddenly heated it is partially dissociated into tungsten trioxide and oxytetrachloride; and H. Schiff also noted that at a high temp. this decomposition occurs. F. Wöhler, J. B. von Borck, C. W. Blomstrand, and H. E. Roscoe said that it usually vaporizes before melting, but A. Riche gave 259° for the m.p. and 256° for the f.p.; and V. Forcher, 265° to 267° for the m.p. L. von Uslar observed that it is reduced to metal when it is heated in a current of hydrogen. H. E. Roscoe said that it is not decomposed by moist air, but F. Wöhler, and V. Forcher observed that moist air slowly decomposes it into hydrochloric acid and hydrated tungsten trioxide. C. G. de Laval also observed that it fumes strongly in air. F. Wöhler, J. J. Berzelius, and A. Riche also observed that the salt is slowly decomposed by water as in the case of moist air; while H. E. Roscoe said that it is not decomposed by cold water; and after many evaporations with water, the residue is not free from chlorine. V. Forcher observed that alkali-lye dissolves the dioxydichloride slowly in the cold, and rapidly when heated. J. J. Berzelius found that conc. hydrochloric acid extracts some tungsten trioxide from the salt. At ordinary temp., ammonia gas reacts giving off fumes of ammonium chloride; and the residue was found by S. Rideal to contain only a little nitrogen, and to be mainly tungsten dioxide, while E. F. Smith and O. L. Shinn observed that $W_4N_4O_4H_2$ is formed; with liquid ammonia, A. Rosenheim and F. Jacobsohn observed the formation of brown tungsten triamminoxide, $WO_3.3NH_3$; and F. Wöhler observed that with aq. ammonia, there is a hissing noise and the development of heat. H. Schiff observed that phosphorus pentachloride converts it into the oxytrichloride. B. Kalischer found that owing to the insolubility of the dioxydichloride in all solvents tried, he was unable to prepare complex salts. Soln. of tungsten trioxide in alcoholic hydrochloric acid, when treated with pyridinium or quinolinium chlorides, yield acicular crystals of $WO_2Cl_2.3C_5H_5N.HCl$, and $WO_2Cl_2.3C_9H_7N.HCl$. R. F. Bernhardi-Grisson obtained similar products.

S. M. Tanatar and E. Kurowsky[3] treated a soln. of sodium tungstate with beryllium chloride, and obtained precipitates of **beryllium chlorotungstates** of variable composition, $BeO.mBeCl_2.nBeWO_4$, insoluble in water and organic solvents, and sparingly soluble in acids. P. Didier found that yellow, channelled crystals of **cerium chlorotungstates,** are formed when equal parts of normal sodium tungstate and anhydrous cerium chloride are heated, with or without fusion in an inert atmosphere. If the cerium chloride be in excess, yellow or red hexagonal plates are formed. The salt may also be prepared by passing hydrogen chloride over a mixture of heated cerium and tungsten oxides.

References.

[1] B. Kalischer, *Zur Kenntnis der Halogenide des höherwertigen Wolfram und Molybdäns*, Berlin, 1902; C. G. de Laval, *Ber.*, **6**. 1464, 1873; *Om Wolfram*, Upsala, 1872; O. O. Collenberg, *Zeit. anorg. Chem.*, **102**. 247, 1918; *Arkiv Kemi Min. Geol.*, **7**. 5, 1918; *Zeit. Elektrochem.*, **31**. 555, 1925; O. Olsson, *Ber.*, **46**. 566, 1913; P. Ray and J. Dasgupta, *Journ. Indian Chem. Soc.*, **5**. 519, 1928; P. Ray and H. G. Bhar, *ib.*, **5**. 497, 1928.

[2] F. Wöhler, *Ann. Chim. Phys.*, (2), **29**. 43, 1823; *Quart. Journ. Science*, **20**. 177, 1826; *Phil. Mag.*, **66**. 263, 1825; *Pogg. Ann.*, **2**. 345, 1924; B. Kalischer, *Zur Kenntnis der Halogenide des höherwertigen Wolframs und Molybdäns*, Berlin, 1902; A. Riche, *Recherches sur le tungstène et ses composés*, Paris, 1857; *Ann. Chim. Phys.*, (3), **50**. 5, 1856; H. O. Schulze, *ib.*, (2), **21**. 441, 1880; H. E. Roscoe, *Liebig's Ann.*, **162**. 359, 1872; *Proc. Manchester Lit. Phil. Soc.*, **11**. 79, 1872; *Bull. Soc. Chim.*, (2), **25**. 61, 1873; *Chem. News*, **25**. 61, 73, 90, 1873; R. F. Bernhardi-Grisson, *Die kathodische Reduktion der Wolframsäure*, Berlin, 1910; C. W. Blomstrand, *Journ. prakt. Chem.*, (1), **82**. 421, 1861; (1), **89**. 238, 1863; J. J. Berzelius, *Ann. Phil.*, **3**. 245, 1814; *Schweigger's Journ.*, **16**. 476, 1816; *Pogg. Ann.*, **4**. 147, 1825; **8**. 267, 1826; *Ann. Chim. Phys.*, (2), **17**. 13, 1821; F. J. Malaguti, *Ann. Chim. Phys.*, (2), **60**. 271, 1835; J. B. von Borck, *Oefvers. Akad. Förh.*, **8**. 149, 1851; *Journ. prakt. Chem.*, (1), **54**. 254, 1851; E. H. Ehrenfeld, *Journ. Amer. Chem. Soc.*, **17**. 381, 1895; E. F. Smith and F. Fleck, *Journ. Amer. Chem. Soc.*, **21**. 1007, 1899; C. G. de Laval, *Ber.*, **6**. 1464, 1873; *Om Wolfram*, Upsala, 1872; V. Forcher, *Journ. prakt. Chem.*, (1), **86**. 227, 1862; *Bull. Soc. Chim.*, (2), **5**. 197, 1863; *Sitzber. Akad. Wien*, **44**. 165, 1861; S. Rideal, *Journ. Chem. Soc.*, **55**. 41, 1889; H. Debray, *Compt. Rend.*, **60**. 820, 1865; O. Ruff and F. Eisner, *Ber.*, **38**. 742, 1905; O. Ruff, F. Eisner and W. Heller, *Zeit. anorg. Chem.*, **52**. 263, 1907; E. F. Smith and O. L. Shinn, *ib.*, **4**. 381, 1893; E. F. Smith and V. Oberholtzer, *ib.*, **5**. 63, 1894; A. Rosenheim and F. Jacobsohn, *ib.*, **50**. 306, 1906; A. Bonnet, *L'Instit.*, **5**. 46, 1837; *Compt. Rend.*, **4**. 198, 1837; H. Schiff, *Liebig's Ann.*, **102**. 111, 1856; **117**. 94, 1861; **197**. 185, 1879; G. Rauter, *ib.*, **270**. 236, 1892; N. Teclu, *ib.*, **187**. 255, 1877; A. Kremer, *ib.*, **70**. 297,

1849; J. Persoz, *Compt. Rend.*, **28**. 86, 389, 1849; C. Gerhardt and L. Chiozza, *ib.*, **36**. 1054, 1853; H. E. Quantin, *ib.*, **104**. 223, 1887; **106**. 1075, 1888; R. Weber, *Pogg. Ann.*, **107**. 375, 1859; *Journ. prakt. Chem.*, (1), **76**. 406, 1859; *Chem. Gaz.*, **17**. 249, 1859; H. Rose, *Pogg. Ann.*, **40**. 395, 1837; A. Vosmaer, *Zeit. anal. Chem.*, **28**. 324, 1889; W. Hampe, *Chem. Ztg.*, **12**. 106, 1888; C. W. Watts and C. A. Bell, *Journ. Chem. Soc.*, **33**. 442, 1878; L. von Uslar, *Beiträge zur Kenntnis des Wolframs und Molybdäns*, Göttingen, 1855; *Liebig's Ann.*, **94**. 255, 1855; K. Lindner, *Ber.*, **55**. B, 1485, 1922; F. Bourion, *Ann. Chim. Phys.*, (8), **21**. 58, 1910; C. Matignon and F. Bourion, *Compt. Rend.*, **138**. 631, 760, 1904; P. Camboulives, *ib.*, **150**. 175, 1910; A. Michael and A. Murphy, *Amer. Chem. Journ.*, **44**. 382, 1910; R. D. Hall, *Journ. Amer. Chem. Soc.*, **26**. 1244, 1904; V. I. Spitzin and L. Kaschtanoff, *Zeit. anorg. Chem.*, **157**. 141, 1926.

[3] S. M. Tanatar and E. Kurowsky, *Journ. Russ. Phys. Chem. Soc.*, **41**. 813, 1909; P. Didier, *Compt. Rend.*, **102**. 823, 1889.

§ 21. Tungsten Bromides and Oxybromides

H. E. Roscoe[1] reported **tungsten dibromide,** WBr_2, to be formed by passing hydrogen over tungsten pentabromide heated in a bath of molten zinc. If the temp. is too low, say 350°, the product is not homogeneous. The pentabromide and oxybromide and bromine may distil over, and the dibromide remains as a bluish-black powder. It behaves towards water and nitric acid vapour like the corresponding dichloride. F. W. Bergstrom observed that a slightly soluble ammoniobasic bromide is formed when the dibromide is treated with liquid ammonia.

J. B. von Borck first prepared impure **tungsten pentabromide,** WBr_5, and A. Riche also obtained it but regarded it as a hexabromide. C. W. Blomstrand showed that it is really the salt of quinquevalent tungsten. Analyses supporting this view were made by J. B. von Borck, C. W. Blomstrand, H. E. Roscoe, and E. Defacqz. J. B. von Borck, A. Riche, and H. E. Roscoe obtained it by passing the vapour of bromine, preferably diluted with carbon dioxide, over red-hot tungsten. All traces of moisture and air must be rigorously excluded. The product is purified from any traces of oxybromide which might be present by repeated sublimation. The temp. of formation is higher than is needed for the pentachloride, and the union is not attended by incandescence. E. Defacqz obtained it by passing dry hydrogen bromide, freed from air, over tungsten hexabromide at 300°—the reaction begins at about 250°. H. E. Roscoe described the crystals as dark brown needles; J. B. von Borck said that the crystals are black with a blue or violet tint; and E. Defacqz, that the sublimate consists of fan-like aggregates of dark needles. J. B. von Borck said that the vapour is dark purple red, almost black, H. E. Roscoe, dark brown. J. B. von Borck found that the pentabromide sublimes almost at its m.p. A. Riche said that it melts to a black, oily liquid which on cooling solidifies to a crystalline mass. H. E. Roscoe gave 276° for the m.p., and 273° for the f.p.; and added that it boils at 333° and decomposes when distilled forming bromine and a lower bromide. E. Defacqz said that it can be volatilized without decomposition in carbon dioxide. E. Defacqz, and H. E. Roscoe found that the pentabromide is reduced to the dibromide by hydrogen at 350°, and at higher temp. to the metal. A. Riche said that when heated in oxygen, it forms a sublimate of the dioxydibromide, and E. Defacqz, that it is decomposed by oxygen into a mixture of oxybromide and tungsten trioxide. J. B. von Borck, A. Riche, C. W. Blomstrand, H. E. Roscoe, and E. Defacqz found that it is very hygroscopic, and fumes in air; it is decomposed by moist air forming hydrogen bromide and blue tungsten oxide; it is also hydrolyzed by water with which it reacts with a hissing noise and the development of much heat. E. Defacqz added that the pentabromide is readily attacked by alkali-lye or fused alkalies, as well as by fused alkali nitrates, carbonates, or hydrosulphates. J. B. von Borck said that some hydrogen is developed when the pentabromide dissolves in alkali-lye. E. Defacqz added that when the pentabromide is heated with chlorine, it forms the hexachloride. Conc. hydrofluoric acid dissolves it, and it forms with conc. hydrochloric acid a blue soln.—the dil. acid acts like water. Dry hydrogen bromide does not decompose it at 300°; and dry fuming hydrobromic acid partially dissolves it. Hydrogen iodide decomposes the pentabromide at 400°, forming an iodide. Sulphur decomposes it forming the sulphide; hydrogen sulphide also converts it into sulphide; conc. sulphuric acid does not act in the cold, but the dil. acid precipitates the blue oxide. The pentabromide is oxidized by nitric acid into tungsten trioxide; phosphorus, and phosphine convert it into the phosphide. A. Riche found that the pentabromide decomposes organic substances, rapidly forming hydrogen bromide and blue tungsten oxide. E. Defacqz added that the pentabromide is soluble in alcohol, ether, carbon tetrachloride, chloroform, bromoform, benzene, and turpentine; if these solvents are not thoroughly dried, blue tungsten oxide may be formed. F. W. Bergstrom observed that a liquid ammonia soln. of tungsten pentabromide in contact with potassamide for several days furnishes *tungsten potassimidamide*, $W(NK)_2NH_2$.

According to H. A. Schaffer and E. F. Smith, **tungsten hexabromide,** WBr_6, is obtained by gently warming tungsten in dry bromine vapour carried along by nitrogen purified by passage through chromous acetate, sulphuric acid, and phosphorus pentoxide. Tungsten hexabromide forms bluish-black, crystalline masses, melts readily, and when carefully resublimed forms blue-black needles. It is decomposed when heated at a high temp., fumes when brought into contact with the air, is decomposed by water with the formation of a blue oxide, and dissolves in aq. ammonia to a colourless soln.

E. Defacqz found that when liquid hydrogen bromide is allowed to act on tungsten hexachloride at ordinary temp., it yields **tungsten trichlorotribromide,** WCl_3Br_3, and at 60° to 70°, **tungsten trichloroenneabromide,** $WBr_3.W_3Cl_3Br_6$, or $W_2Cl_3Br_9$. The latter compound forms small, olive-green crystals which melt at 232° and dissolve in many organic solvents. It is very unstable, alters rapidly when exposed to air, is immediately decomposed by water, and by steam at 200°, and is readily attacked by hydrogen, oxygen, chlorine, sulphur, phosphorus, halogen hydracids, hydrogen sulphide, nitric and sulphuric acids, alkalies, oxidizing mixtures, and potassium hydrosulphate.

H. P. von Beck prepared some oxybromides—$R'_2(WOBr_5)$; $R'\{WOBr_4(H_2O)\}$; and $R'(WOBr_4)$—analogous to the oxychlorides obtained by O. O. Collenberg. By treating 5 grms. of potassium oxalatotungstite with 35 c.c. of hydrobromic acid at 50°, and afterwards adding rubidium sulphate he obtained **rubidium pentabromotungstite,** $Rb_2(WOBr_5)$, in olive-green octahedra; if cæsium sulphate be employed, **cæsium pentabromotungstite,** $Cs_2(WOBr_5)$, is formed in greenish-yellow octahedra. By adding 17 grms. of ammonium oxalatotungstite to a soln. of 180 c.c. of hydrobromic acid and 3·5 grms. of ammonium bromide at 55°, **ammonium pentabromotungstite,** $(NH_4)_2(WOBr_5)$, was formed in olive-green octahedra.

By treating 10 grms. of potassium oxalatotungstite with 80 c.c. of hydrobromic acid at 55°, **pyridinium tetrabromotungstite,** $(C_5H_5NH)(WOBr_4)$, was formed in brownish-green quadratic plates. If soln. of 10 grms. of sodium oxalatotungstite in 75 c.c. of hydrobromic acid and of 8 grms. of tetraethylammonium bromide in 40 c.c. of hydrobromic acid be mixed, **tetraethylammonium tetrabromoaquotungstite,** $(C_2H_5)_4N\{WOBr_4(H_2O)\}$, is formed in pale green, microscopic scales.

According to A. Bonnet, when bromine vapour is passed over a mixture of tungsten trioxide and carbon, **tungsten oxytetrabromide,** $WOBr_4$, is formed. C. W. Blomstrand obtained it by heating tungsten in bromine vapour mixed with a little air, and by rapidly heating the dioxydibromide which then forms tungsten trioxide and oxytetrabromide. H. E. Roscoe obtained it by the action of bromine vapour on a heated mixture of tungsten and tungsten dioxide. The oxytetrabromide is usually accompanied by less volatile dioxydibromide from which it can be separated by sublimation. Analyses were made by A. Bonnet, J. B. von Borck, C. W. Blomstrand, and H. E. Roscoe. J. B. von Borck thought that the product was tungsten tetrabromide, but C. W. Blomstrand showed that it is the oxytetrabromide. The brownish-black needles form a heavy, yellowish-red vapour; the salt can be resublimed in a current of carbon dioxide. It melts at 277°, and boils at 327°. It is very hygroscopic; and is decomposed by moist air, and water into hydrobromic acid and pseudomorphous tungsten trioxide.

J. B. von Borck, C. W. Blomstrand, and H. E. Roscoe prepared **tungsten dioxydibromide,** WO_2Br_2, by the action of bromine vapour—not free from air—on heated tungsten dioxide, blue tungsten oxide, tungsten trisulphide, or a mixture of tungsten trioxide and carbon; H. E. Roscoe, by passing the vapour of tungsten pentabromide over the trioxide; and H. O. Schulze, by heating tungsten trioxide with bromides—*vide supra,* the dioxydichloride. A. Bonnet by working as in the case of the preceding compound at a lower temp., thought that $W_2O_5.2WBr_2$ is formed, but C. W. Blomstrand could not verify this. The analyses of J. B. von Borck, and H. E. Roscoe agree with the formula WO_2Br_2. The pale yellow vapour, said H. E. Roscoe, condenses to black prismatic crystals, which on cooling, appear pale red, and furnish a yellow bromide. J. B. von Borck, and C. W. Blomstrand said that the quadratic plates are a brassy yellow resembling muscovite gold. H. E. Roscoe, and J. B. von Borck said that the salt volatilizes at a red-heat without melting, and with a partial decomposition into tungsten oxytetrachloride and trioxide. H. E. Roscoe found that the salt is not decomposed by cold water; and J. B. von Borck, that it is hydrolyzed in moist air and by water to form hydrobromic acid, and hydrated tungsten trioxide.

REFERENCES.

[1] H. E. Roscoe, *Liebig's Ann.*, **162**. 359, 1872; *Proc. Manchester Lit. Phil. Soc.*, **11**. 79, 1872; *Bull. Soc. Chim.*, (2), **25**. 61, 1873; *Chem. News*, **25**. 61, 73, 90, 1873; J. B. von Borck, *Oefvers. Akad. Förh.*, **8**. 149, 1851; *Journ. prakt. Chem.*, (1), **54**. 254, 1851; A. Riche, *Recherches sur le tungstène et ses composés*, Paris, 1857; *Ann. Chim. Phys.*, (3), **50**. 5, 1856; C. W. Blomstrand, *Journ. prakt. Chem.*, (1), **82**. 421, 1861; (1), **89**. 238, 1863; E. Defacqz, *Compt. Rend.*, **128**. 610, 1232, 1899; **129**. 515, 1899; *Ann. Chim. Phys.*, (7), **22**. 244, 1901; *Contribution à l'étude du tungstène et de ses composés*, Paris, 1901; H. A. Schaffer and E. F. Smith, *Journ. Amer. Chem. Soc.*, **18**. 1098, 1896; *Chem. News*, **75**. 37, 1897; A. Bonnet, *L'Instit.*, **5**. 46, 1837; *Compt. Rend.*, **4**. 198, 1837; H. O. Schulze, *Ann. Chim. Phys.*, (2), **21**. 441, 1880; F. W. Bergstrom, *Journ. Amer. Chem. Soc.*, **47**. 2317, 1925; O. O. Collenberg, *Zeit. Elektrochem.*, **31**. 555, 1925; *Zeit. anorg. Chem.*, **102**. 247, 1918; H. P. von Beck, *ib.*, **196**. 85, 1931.

§ 22. Tungsten Iodides and Oxyiodides

No *tungsten hexaiodide,* WI_6, has been prepared, nor have *tungsten oxyiodides* been obtained. According to A. Riche,[1] the vapour of iodine attacks tungsten superficially, and the sublimed product is difficult to purify; it appears to contain a brown iodide, and green scales of another iodide. J. B. von Borck observed that tungsten trioxide dissolves in hydriodic acid, and when the soln. is evaporated, in vacuo, it is decomposed. No tungsten iodide is formed when the vapour of tungsten chloride is passed over molten potassium iodide or silver iodide, or when it is brought in contact with the vapour of mercuric iodide, ammonium iodide, or hydrogen iodide. H. E. Roscoe reported that **tungsten diiodide,** WI_2, is formed when iodine vapour is passed over red-hot tungsten or tungsten dioxide. The diiodide collects quite near to the heated portion of the tube in small scales which cannot be volatilized without decomposition. E. Defacqz obtained it by passing chlorine over tungsten at a dark-red heat; driving out the chlorine by dried carbon dioxide; and allowing dried hydrogen iodide to act on the sublimed tungsten hexachloride at 400°. At first some iodine is set free, and the product is accordingly washed with carbon disulphide, dried in air, washed with alcohol, and dried in air, first at 95° and then at 100°. According to E. Defacqz, tungsten diiodide is an amorphous, brown powder of sp. gr. 6·9 at 18°, and insoluble in water, alcohol, or carbon disulphide. It is infusible and non-volatile; when heated in air, it is oxidized, and when heated above 500° in hydrogen it is reduced. Chlorine decomposes it at about 250°, and bromine at about 350°. Hydrogen iodide reduces it at 500° to 600°, and it is also attacked by carbon dioxide at this temp. Sulphur and phosphorus at 500° convert the iodide into sulphide and phosphide respectively, and boiling water gradually converts it into the blue oxide. Hydrochloric and hydrofluoric acids attack the iodide very slowly, but boiling nitric or sulphuric acid, or aqua regia, converts it into tungstic anhydride. Potash-lye or fused potassium hydroxide, alkali carbonates, or mixtures of alkali carbonates and nitrates readily oxidize the iodide.

According to E. Defacqz, **tungsten tetraiodide,** WI_4, is obtained by the action of an excess of liquid hydrogen iodide on tungsten hexachloride at 110°. It is a black, crystalline substance of sp. gr. 5·2 at 18°; insoluble in water, ether, chloroform, and turpentine, but soluble in absolute alcohol; it does not melt, and does not sublime without decomposing. Hydrogen reduces it below a red-heat; chlorine displaces the iodine at the ordinary temp.; and bromine displaces it at 100°. Water decomposes it slowly in the cold, and rapidly on boiling, and it is readily attacked by dil. hydrochloric and sulphuric acids, and by nitric acid and aqua regia, which convert it into tungstic acid. Alkali hydroxides and carbonates, whether in soln. or fused, and fused potassium hydrosulphate also readily decompose the tetraiodide.

References.

[1] A. Riche, *Recherches sur le tungstène et ses composés*, Paris, 1857; *Ann. Chim. Phys.*, (3), **50**. 5, 1856; J. B. von Borck, *Oefvers Akad. Förh.*, **8**. 149, 1851; *Journ. prakt. Chem.*, (1), **54**. 254, 1851; H. E. Roscoe, *Liebig's Ann.*, **162**. 359, 1872; *Proc. Manchester Lit. Phil. Soc.*, **11**. 79. 1872; *Bull. Soc. Chim.*, (2), **25**. 61, 1873; *Chem. News*, **25**. 61, 73, 90, 1873; E. Defacqz, *Compt. Rend.*, **128**. 610, 1232, 1899; **129**. 515, 1899; *Ann. Chim. Phys.*, (7), **22**. 244, 1901; *Contribution à l'étude du tungstène et de ses composés*, Paris, 1901.

§ 23. The Tungsten Sulphides

J. B. von Borck[1] obtained **tungsten disulphide,** WS_2, by melting a mixture of the constituent elements; J. J. Berzelius passed sulphur vapour or hydrogen sulphide over red-hot tungsten trioxide. The action is incomplete, and A. Riche recommended mixing the tungsten trioxide with carbon, or passing the vapour of carbon disulphide over the red-hot trioxide. J. J. Berzelius, and J. B. von Borck heated a mixture of tungsten trioxide and an excess of mercuric sulphide in a fireclay crucible contained in a larger crucible packed with carbon. When ammonium sulphotungstate is heated in a current of carbon dioxide, E. Corleis found that porous pseudomorphs of tungsten disulphide are formed. F. J. Faktor obtained the disulphide by the action of tungsten trioxide on sodium thiosulphate. L. von Uslar heated a mixture of tungsten trisulphide and potassium cyanide and extracted the soluble matter with water; A. Riche melted a mixture of potassium tungstate and tungsten trioxide, and added sulphur—after half an hour's fusion, the cold mass was extracted with water. E. Defacqz melted at a dull red-heat an intimate mixture of dry potassium carbonate, sulphur, and tungsten trioxide (138 : 558 : 464), and when completely fused, the cold mass was powdered and extracted with water. When hydrogen sulphide free from air acts on tungsten hexachloride heated to 375° and the temp. is raised to 550°, and the product cooled in hydrogen sulphide, E. Defacqz found that tungsten disulphide is formed.

Analyses were made by E. Defacqz, J. J. Berzelius, L. von Uslar, E. Corleis, and A. Riche, and the results were in agreement with the formula WS_2. R. C. Wells and B. S. Butler found the disulphide occurring as a mineral which they called **tungstenite** in the Emma mine, of the Cottonwood district, Salt Lake Co., Utah. It occurs in feathery flakes resembling graphite. It is lead-grey in colour; opaque with a metallic lustre; and is soft enough to mark paper. J. J. Berzelius described the disulphide as a greyish-black, soft powder; and E. Defacqz, as a black, scaly mass, or as friable crystals with a blue reflex. A. E. van Arkel found that the

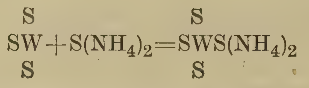
X-radiogram of tungsten disulphide corresponded with a space-lattice resembling that of molybdenite (*q.v.*), with two mols per unit cell. The unit cell has a base 3·18 A., and a height 12·5 A. The S-atoms form layers of trigonal pyramids which are 3·63 A. in length along the pyramid edges and 3·18 A. along the basal edges. The structure was discussed by J. W. Gruner. According to E. Defacqz, the sp. gr. is 7·5 at 10°. M. Picon found that the sulphide is dissociated at 1200° to 1300°, and not volatilized at 2000°. R. C. Wells and B. S. Butler gave 7·4 for the sp. gr. of tungstenite. A. Karl studied the triboluminescence of tungsten sulphide. W. W. Coblentz found that tungsten sulphide is not photoelectrically sensitive. J. J. Berzelius said that when roasted in air it forms tungsten trioxide, and in the absence of air, E. Defacqz said that it can be heated to redness without change, while in the electric furnace it gradually loses its sulphur without melting. A. Riche observed that when heated in hydrogen it is reduced to metal, and E. Corleis said that the reduction is complete in about 7 hrs. at the temp. of a blowpipe flame; and E. Defacqz added that the reaction begins at about 800°. N. Parravano and G. Malquori found the equilibrium constant $K=p_{H_2S}/p_{H_2}$ for the reaction $2H_2+WS_2 \rightleftharpoons W+2H_2S$ over the range of temp. 795° to 1065°; and the calculated heat of formation of WS_2 is 73·4 Cals. They also gave for the dissociation press., $\log p_{S_2}=-10{\cdot}453$ at 600°; $-6{\cdot}938$ at 795°; $-5{\cdot}611$ at 895°; $-4{\cdot}603$ at 985°; and $-4{\cdot}642$ at 1065°. Fluorine attacks it at ordinary temp.; chlorine, at 400° with the formation of the hexachloride; whilst the reaction with bromine is incomplete at 700°. Hydrogen chloride has no action on the disulphide. Mineral acids employed singly are without action, but it is attacked by mixtures of nitric acid with hydrofluoric or hydrochloric acid. J. J. Berzelius found that the disulphide is oxidized by aqua regia to sulphuric acid and tungsten trioxide; R. C. Wells and B. S. Butler found that tungstenite is not attacked by hydrochloric or nitric acid but is decomposed by aqua regia. E. Defacqz found that molten alkali hydroxides or carbonates readily dissolve the disulphide, and so does a fused mixture of potassium nitrate and carbonate. L. Weiss reduced it to the metal by heating it with lime in an electric furnace.

L. von Uslar obtained **tungsten trisulphide,** WS_3, by melting wolframite with powdered carbon, sulphur, and sodium carbonate (1 : 0·2 : 3) at a dull red-heat, extracting the product with water, and precipitating the compound by the addition of sulphuric acid. J. J. Berzelius dissolved tungsten trioxide in a soln. of potassium hydrosulphide, and precipitated the compound by means of an acid; he also saturated a soln. of ammonium tungstate with hydrogen sulphide, added an acid to the soln., and washed the precipitate with cold water. J. B. von Borck said that all these products contain tungsten trioxide and much water. The trisulphide can be obtained of a high degree of purity by protecting it from atm. air while being prepared. E. Corleis also obtained the trisulphide as a chocolate brown powder by adding hydrochloric acid to a soln. of ammonium sulphotungstate in an apparatus from which atm. air is excluded. The product was washed with aq. hydrogen sulphide in an atmosphere of carbon dioxide and dried at 100° in a similar atmosphere.

Tungsten trisulphide is a black or dark brown powder, which when heated in a closed vessel was found by J. J. Berzelius to form the disulphide; and when boiled with water in a retort it gives off some hydrogen sulphide. Water dissolves a little trisulphide, particularly warm water, and it is precipitated from the yellow soln. by acids, or ammonium chloride. E. Corleis emphasized its acid character by showing that it dissolves in a cold conc. soln. of an alkali carbonate with the evolution of carbon dioxide; it also forms dark brown soln. with alkali hydroxides or hydrosulphides from which no crystals can be obtained. J. J. Berzelius added that the soln. in alkali hydroxide or carbonate contains alkali tungstate, and sulphotungstate—and probably colloidal tungsten trisulphide; when dissolved in soln. of the alkali sulphides, hydrogen sulphide is evolved; and with the basic metal sulphides it forms **sulphotungstates,** R_2WS_4, from which soln. an excess of acid precipitates tungsten trisulphide with the evolution of hydrogen sulphide. Aq. ammonia dissolves the dried sulphide very slowly, and the freshly precipitated, moist sulphide, quickly.

As just indicated, J. J. Berzelius observed that when the freshly-precipitated trisulphide is washed with water, it appears to dissolve, forming a yellow soln. of what is now called **colloidal tungsten trisulphide.** According to C. Winssinger, a dark brown colloidal soln. of the trisulphide is obtained by adding to a dil. soln. of sodium sulphotungstate rather more hydrochloric acid than is needed to liberate tungsten trisulphide. Its colour is orange, and the soln. can be obtained quite clear. The absorption spectrum of the reddish-brown soln. shows a dark band from the extreme violet to the green. The extreme red is feeble, and the visible part of the spectrum is also feeble. The soln. becomes turbid, or a precipitate is formed by boiling, by adding conc. hydrochloric acid, ammonium chloride, or other salts; or by dialysis. If precipitated, the sulphide can be washed by decantation, and as the impurities are removed the sulphide is again peptized so as to re-form a colloidal soln. Freshly precipitated trisulphide is easily oxidized so that air must be excluded during these operations.

The normal sulphotungstates, R_2WS_4, are prepared by dissolving tungsten trisulphide in the metal hydrosulphide; by the prolonged action of hydrogen sulphide on normal tungstates; and by double decomposition. The alkali sulphotungstates are soluble and crystalline; some of the alkaline earth and metal sulphotungstates form gummy or gelatinous masses. According to C. Scheibler, if an aq. soln. of metatungstic acid be saturated with hydrogen sulphide, and neutralized with ammonia, or ammonium sulphide, blue sulphur separates out, and after a time bluish-black, cubic crystals are formed. They oxidize in air, and decolorize. They are very unstable. A. Werner discussed the formula, $(NH_4)_2[WS_4]$:



$$\underset{\mathrm{S}}{\overset{\mathrm{S}}{\mathrm{SW}}}+\mathrm{S(NH_4)_2}=\underset{\mathrm{S}}{\overset{\mathrm{S}}{\mathrm{SW}}}\mathrm{S(NH_4)_2}$$

J. J. Berzelius obtained **ammonium sulphotungstate,** $(NH_4)_2WS_4$, in yellowish-red crystals by saturating a conc. soln. of ammonium tungstate with hydrogen sulphide; on evaporating the mother-liquor, yellow plates of a double salt of tungstate and sulphotungstate are formed. E. Corleis obtained this salt by the action of hydrogen sulphide for 5 or 6 hrs. on a soln. of 10 grms. of hydrated tungsten trioxide in 100 c.c. of aq. ammonia of sp. gr. 0·94, and 20 c.c. of water, and allowing the liquid to stand in a closed vessel for crystallization. In about 8 days, the orange-yellow crystals can be washed successively with a soln. of hydrogen sulphide, alcohol, and ether, and finally dried in vacuo over phosphorus pentoxide. The mother-liquid containing dioxydisulphotungstate can be again saturated with hydrogen sulphide, and treated as before. The precipitation is accelerated if one-third to half a vol. of alcohol is added. H. Vater said that the pale orange-yellow, rhombic bipyramidal crystals have the axial ratios $a:b:c=0·7783:1:0·5675$; the (010)-cleavage is complete, the (001)-cleavage clear. The crystals are isomorphous with those of the corresponding molybdenum salt. J. J. Berzelius, and E. Corleis found that the crystals decrepitate when heated, and then give off water and ammonium sulphide, leaving tungsten disulphide as a residue, pseudomorphous after ammonium sulphide. The salt is fairly stable when dry, but when moist it is unstable. It is slowly reduced to metal when heated in hydrogen. It is freely soluble in water, and in aq. ammonia; and it is precipitated from these soln. by the addition of alcohol. The aq. soln. slowly decomposes in air. L. Storch discussed the solubility of the metal sulphides in a soln. of ammonium sulphotungstate.

J. J. Berzelius said that **sodium sulphotungstate,** Na_2WS_4, crystallizes with difficulty from an aq. soln. of its components, but if the aq. alcoholic soln. be spontaneously evaporated the salt is obtained in crystals. E. Corleis prepared it by adding sodium hydrosulphide to a conc. soln. of the ammonium salt. The crystals contain some isomorphous ammonium salt; they deliquesce rapidly in air, and resemble the crystals of the potassium salt. J. J. Berzelius prepared **potassium sulphotungstate,** K_2WS_4, by saturating an aq. soln. of potassium tungstate with hydrogen sulphide and evaporating the soln. in vacuo over potassium carbonate, or in air; and by evaporating a soln. of tungsten trioxide or trisulphide in potassium hydrosulphide, or of tungsten trisulphide in potassium hydroxide. E. Corleis found that the salt is precipitated on adding potassium hydrosulphide and alcohol to a soln. of ammonium sulphotungstate. By recrystallization of the salt from a soln. of potassium hydrosulphide, it can be completely freed from the isomorphous ammonium sulphotungstate. E. Kalkowsky said that the yellow, rhombic bipyramids have the axial ratios $a:b:c=0{\cdot}7495:1:0{\cdot}5665$; and that the (010)-cleavage is incomplete. J. J. Berzelius found that the crystals, in the absence of air, melt to a dark brown liquid which solidifies on cooling to a brownish-yellow mass. The salt is freely soluble in water, and on adding alcohol to the brownish-yellow aq. soln., cinnabar-red prisms are deposited, but the precipitation is not complete, for the salt is slightly soluble in alcohol. If an acid be added to the aq. soln., *potassium sulphoditungstate*, $K_2S.2WS_3$, is formed, and deposited as a black mass when the dark brown soln. is evaporated. J. J. Berzelius described a complex salt, formed by fusing a mixture of sulphur and potassium tungstate, which was considered to be $K_2WO_4.K_2WS_4$, presumably an isomorphous admixture.

J. J. Berzelius described **copper sulphotungstate** as a dark brown precipitate; **silver sulphotungstate** as a dark brown, almost black, precipitate; and **gold sulphotungstate,** $Au_4(WS_4)_3$, as a dark brown mixture of aurous and auric salts on adding a soln. of the metal salt to a soln. of potassium sulphotungstate. He also obtained calcium sulphotungstate by treating freshly prepared calcium tungstate, suspended in water, with hydrogen sulphide, and evaporating the yellow soln., or by dissolving tungsten trisulphide in a hot soln. of calcium disulphide, or hydrosulphide. The pale yellow, amorphous mass is easily soluble in water, and in alcohol. With an excess of tungsten trisulphide it forms a reddish-brown, non-crystallizable soln. which with ammonia gives a pale yellow precipitate. The corresponding **strontium sulphotungstate** and **barium sulphotungstate** were similarly obtained. No precipitate of **beryllium sulphotungstate** is obtained when a soln. of a beryllium salt is treated with potassium sulphotungstate; **magnesium sulphotungstate** is prepared like the barium salt, and the aq. soln., in vacuo, dries to a gummy mass soluble in water and alcohol. F. Rodolico obtained a complex salt, $MgWS_4.2X.10H_2O$, with hexamethylenetetramine. J. J. Berzelius prepared **zinc sulphotungstate** which forms a pale yellow, pulverulent precipitate; and with **cadmium sulphotungstate** which forms a lemon-yellow powder; mercurous salts give a black precipitate of more or less decomposed **mercurous sulphotungstate;** and mercuric salts, yellow **mercuric sulphotungstate** which, after drying, is dark red.

When an aluminium salt soln. is treated with potassium sulphotungstate, no **aluminium sulphotungstate** is precipitated; similarly with **yttrium sulphotungstate;** but a soln. of a cerous salt in 24 hrs. gives a yellow precipitate of **cerous sulphotungstate.** Stannous salt soln. gives a brown, flocculent precipitate of **stannous sulphotungstate,** $SnWS_4$; a soln. of a stannic salt, greyish-yellow **stannic sulphotungstate,** a lead salt, dark brown **lead sulphotungstate,** $PbWS_4$; whilst a dark brown **bismuth sulphotungstate,** $Bi_2(WS_4)_3$; brown **vanadyl sulphotungstate;** yellow **manganese sulphotungstate,** $MnWS_4$; deep yellow **ferrous sulphotungstate,** $FeWS_4$; dark brown **ferric sulphotungstate,** $Fe_2(WS_4)_3$; dark brown **cobalt sulphotungstate,** $CoWS_4$; similarly with **nickel sulphotungstate,** $NiWS_4$; dark brown **platinum sulphotungstate,** $Pt(WS_4)_2$, are obtained from soln. of the metal salts concerned.

According to E. Defacqz, if liquid hydrogen sulphide be left in contact with tungsten hexachloride in a sealed tube for 36 hrs., at 60° to 65°, a brown powder of **tungsten hexachloroenneasulphide,** $WCl_6.3WS_3$, is formed. It is insoluble in carbon disulphide, alcohol, and benzene, and is decomposed by water. It burns in air at a red-heat; and is easily attacked by nitric acid, and by fused alkali hydroxide. E. F. Smith and V. Oberholtzer found that if tungsten is heated to redness in the vapour of sulphur monochloride, a red crystalline sublimate of **tungsten octochloroheptasulphide,** $W_2S_7Cl_8$, is formed. The unstable product is considered to be a complex of $W_2S_3Cl_4$ with $2S_2Cl_2$. For the complex $WCl_4.N_4S_4$, *vide supra*, tungsten tetrachloride.

References.

[1] J. J. Berzelius, *Ann. Phil.*, **3**. 245, 1814; *Schweigger's Journ.*, **16**. 476, 1816; *Pogg. Ann.*, **4**. 147, 1825; **8**. 267, 1826; *Ann. Chim. Phys.*, (2), **17**. 13, 1821; J. B. von Borck, *Oefvers Akad. Förh.*, **8**. 149, 1851; *Journ. prakt. Chem.*, (1), **54**. 254, 1851; A. Riche, *Recherches sur le tungstene et ses composés*, Paris, 1857; *Ann. Chim. Phys.*, (3), **50**. 5, 1856; L. von Uslar, *Beiträge zur Kenntnis des Wolframs und Molybdäns*, Göttingen, 1855; *Liebig's Ann.*, **94**. 255, 1855; E. Corleis, *ib.*, **232**. 261, 1886; *Bull. Soc. Chim.*, (2), **47**. 190, 1887; *Ueber die Schwefelverbindungen des Wolframs*, München, 1885; F. J. Faktor, *Pharm. Post.*, **38**. 527, 1905; E. Defacqz, *Ann. Chim. Phys.*, (7), **22**. 239, 1901; *Contribution à l'étude du tungstène et de ses composés*, Paris, 1901; *Compt. Rend.*, **128**. 610, 1899; A. Karl, *ib.*, **146**. 1104, 1908; C. Winssinger, *Bull. Soc. Chim.*, (2), **49**. 452, 1888; *Bull. Acad. Belg.*, (2), **15**. 390, 1888; R. C. Wells and B. S. Butler, *Journ. Washington Acad.*, **7**. 596, 1917; L. Weiss, *Zeit. anorg. Chem.*, **65**. 279, 1910; A. Werner, *ib.*, **9**. 403, 1895; E. F. Smith and V. Oberholtzer, *ib.*, **5**. 66, 1893; E. Kalkowsky, *Zeit. Kryst.*, **13**. 32, 1888; H. Vater, *ib.*, **10**. 392, 1885; A. E. van Arkel, *Rec. Trav. Chim. Pays-Bas*, **45**. 437, 1926; C. Scheibler, *Journ. prakt. Chem.*, (1), **83**. 313, 1861; *Chem. News*, **6**. 181, 1862; L. Storch, *Ber.*, **16**. 2015, 1883; N. Parravano and G. Malquori, *Atti Accad. Lincei*, (6), **7**. 189, 1928; *Gazz. Chim. Ital.*, **58**. 279, 1928; W. W. Coblentz, *Scient. Papers U.S. Bur. Standards*, **18**. 586, 1922; *Various Photoelectric Investigations*, Washington, 596, 1922; M. Picon, *Compt. Rend.*, **189**. 96, 1929; *Bull. Soc. Chim.*, (4), **45**. 907, 1929; J. W. Gruner, *Amer. Min.*, **14**. 173, 470, 1929; F. Rodolico, *Atti Accad. Lincei*, (6), **7**. 660, 1928.

§ 24. The Tungsten Oxysulphides and Sulphates

A series of oxysulphotungstates has been reported by J. J. Berzelius,[1] and E. Corleis, but they have not been closely investigated. They include the oxytrisulphotungstates, R_2WOS_3, the dioxysulphotungstates, $R_2WO_2S_2$, and the trioxysulphotungstates, R_2WO_3S. They are obtained by the action of hydrogen sulphide on the normal tungstates, and by fusion of the normal tungstate with definite proportions of sulphur while protected from air. When a soln. of normal sulphotungstate is mixed with alcohol and ether, and treated with hydrochloric acid, two layers of liquid are formed. The ethereal layer is brown, the aq. layer is colourless and clear; an oxysulphide under similar conditions gives a coloured ethereal layer, and a turbid or milky aq. layer. The normal sulphotungstates do not give a precipitate with zinc sulphate, while the oxysulphotungstates give a precipitate. The *oxytrisulphotungstates* give a lemon-yellow precipitate which forms a reddish-brown soln. with hydrochloric acid; the precipitate with the *dioxydisulphotungstates* is pale yellow, and with hydrochloric acid, the liquid becomes clear and then deposits a dirty blue precipitate; and the *trioxysulphotungstates* give a white precipitate, soluble in hydrochloric acid. This soln. after a time deposits a white precipitate with a bluish tinge. J. W. Retgers said that the intermediate stages between potassium tungstate and sulphotungstate cannot be regarded as isomorphous with the end-members of the series, but they are *selbständige chemische Verbindungen.*

According to E. Corleis, **potassium oxytrisulphotungstate,** $K_2WOS_3.H_2O$, is obtained in quadratic plates by the prolonged action of hydrogen sulphide on potassium tungstate. It dissolves freely in water, deliquesces in a damp atmosphere, and effloresces in a dry atm. The soln. gives a lemon-coloured precipitate with zinc sulphate. The precipitate with zinc sulphate may be *zinc oxytrisulphotungstate.* F. Rodolico prepared **magnesium oxytrisulphotungstate** as a complex salt with hexamethylenetetramine, $MgWOS_3.X.10H_2O$.

If an acid be added to a soln. of alkali tungstate and sulphotungstate,

J. J. Berzelius said that a pale reddish-brown precipitate of tungsten dioxysulphide, WO_2S, is formed; and C. Winssinger added that after tungsten trisulphide has been precipitated from its colloidal soln., the remaining lemon-yellow liquid contains the dioxydisulphide. The individuality of the compound is not well-established.

According to E. Corleis, **ammonium dioxydisulphotungstate,** $(NH_4)_2WO_2S_2$, is produced when hydrogen sulphide is passed into a filtered soln. of 10 grms. of hydrated tungstic trioxide in 40 c.c. of aq. ammonia of sp. gr. 0·90, and 10 c.c. of water, until yellow crystals begin to appear, and after crystallization has ceased, washing the crystals successively with a little water, alcohol, and ether, and drying them over calcium chloride or potassium hydroxide. E. Kalkowsky said that the yellow, triclinic pinacoids have the axial ratios $a:b:c=0{\cdot}760:1:0{\cdot}339$, and $\alpha=90°$, $\beta=92° 10'$, and $\gamma=90°$. The (011)- and $(0\bar{2}1)$-cleavages are clear; there is lamellar twinning. E. Corleis found that the crystals are not hygroscopic; they are stable when dry, but decompose when moist. J. J. Berzelius obtained **potassium dioxydisulphotungstate,** $K_2WO_2S_2.H_2O$, by melting a mixture of the normal potassium tungstate and sulphur in a covered crucible, extracting with water, and evaporating the aq. soln. Lemon-yellow, rectangular plates are formed. The salt can be melted, out of contact with air, without decomposition. It is freely soluble in water. The lemon-yellow aq. soln. is coloured red or reddish-yellow by acids, and it gives no precipitate with alcohol, or with manganous salts. F. Rodolico obtained a complex salt of **magnesium dioxydisulphotungstate** with hexamethylenetetramine, $MgWS_2O_2.2X.10H_2O$. J. J. Berzelius found that the potassium salt forms with a soln. of a lead salt, a yellowish-brown precipitate of **lead dioxydisulphotungstate,** $PbWO_2S_2$.

E. Corleis prepared **potassium trioxysulphotungstate,** $K_2WO_3S.H_2O$, by passing hydrogen sulphide into a conc. soln. of potassium tungstate, until a slight yellow precipitate is formed. The colourless, deliquescent crystals are deposited when the filtered soln. is mixed with five times its vol. of alcohol. With an aq. soln. of the salt, zinc sulphate gives a white precipitate soluble in hydrochloric acid. F. Rodolico obtained a complex salt of **magnesium trioxysulphotungstate** with hexamethylenetetramine, $MgWSO_3.2X.10H_2O$.

J. J. Berzelius[2] obtained a white precipitate presumably a mixture of tungsten trioxide, sulphuric acid, and water when conc. nitric acid acts on tungsten trisulphide. It is very doubtful if the precipitate can be regarded as a *tungsten sulphate.* According to E. D. Desi, if tungsten be heated with conc. sulphuric acid until the evolution of sulphur dioxide has ceased, a blue precipitate and a colourless soln. are formed. If the clear soln. be evaporated a black substance of the composition **tungsten sulphatotrioxide,** $WO_3.SO_3$, is formed. The solid soln. of lead sulphate and tungstate has been previously discussed.

REFERENCES.

[1] J. J. Berzelius, *Ann. Phil.*, **3**. 245, 1814; *Schweigger's Journ.*, **16**. 476, 1816; *Pogg. Ann.*, **4**. 147, 1825; **8**. 267, 1826; *Ann. Chim. Phys.*, (2), **17**. 13, 1821; E. Corleis, *Liebig's Ann.*, **232**. 261, 1886; *Bull. Soc. Chim.*, (2), **47**. 190, 1887; *Ueber die Schwefelverbindungen des Wolframs*, München, 1885; E. Kalkowsky, *Zeit. Kryst.*, **13**. 32, 1888; J. W. Retgers, *Zeit. phys. Chem.*, **10**. 559, 1892; F. Rodolico, *Atti Accad. Lincei*, (6), **7**. 660, 1928; C. Winssinger, *Bull. Soc. Chim.*, (2), **49**. 452, 1888; *Bull. Acad. Belg.*, (2), **15**. 390, 1888.

[2] J. J. Berzelius, *Ann. Phil.*, **3**. 245, 1814; *Schweigger's Journ.*, **16**. 476, 1816; *Pogg. Ann.*, **4**. 147, 1825; **8**. 267, 1826; *Ann. Chim. Phys.*, (2), **17**. 13, 1821; E. D. Desi, *Journ. Amer. Chem. Soc.*, **19**. 213, 1897.

§ 25. Tungsten Carbonates and Nitrates

No *tungsten carbonate* has been prepared; and similarly with *tungsten nitrate.* J. C. G. de Marignac[1] prepared **ammonium nitratometatungstate,** $NH_4NO_3.2\{(NH_4)_2O.4WO_3.2H_2O\}$, by evaporating a mixed, filtered soln. of ammonium paratungstate and nitric acid, or a mixed soln. of ammonium metatungstate and nitrate. The hexagonal crystals lose half their water at 100°; and when heated decrepitate and decompose without melting. J. J. Berzelius saturated a mixed soln. of potassium tungstate and nitrate with hydrogen sulphide, and obtained ruby-red crystals of **potassium nitratosulphotungstate,** $KNO_3.2K_2WS_4$. They explode when heated just as they begin to melt, forming potassium tungstate, and sulphotungstate, and tungsten bisulphide. With sulphuric or hydrochloric acid, hydrogen sulphide is evolved, and if heated, nitric oxide also is given off. The salt is soluble in water, forming a deep red soln., from which alcohol precipitates the salt in crystalline grains. When the soln. is treated with hydrated copper oxide, copper sulphide is precipitated and a soln. of **copper nitratotungstate** is formed. According to E. Péchard, a hot, mixed soln. of barium metatungstate and nitrate furnishes on cooling acicular crystals of **barium nitratometatungstate,** $2Ba(NO_3)_2.BaO.4WO_3.6H_2O$. The crystals effloresce in air; and they are soluble in warm water with partial decomposition. S. M. Tanatar and E. Kurowsky treated a soln. of sodium tungstate with beryllium nitrate and obtained complexes of **beryllium nitratometatungstate,** of variable composition, $BeO.mBe(NO_3)_2.nBeWO_4$, soluble in acids. H. Copaux described **mercurous nitratometatungstate**—*vide supra*, mercury metatungstates; and A. Rosenheim and F. Kohn, V. Forcher, and E. F. Smith, **lead nitratometatungstate**—*vide supra*, lead metatungstates.

REFERENCES.

[1] J. J. Berzelius, *Ann. Phil.*, **3**. 245, 1814; *Schweigger's Journ.*, **16**. 476, 1816; *Pogg. Ann.*, **4**. 147, 1825; **8**. 267, 1826; *Ann. Chim. Phys.*, (2), **17**. 13, 1821; E. Péchard, *ib.*, (6), **22**. 195, 1891; V. Forcher, *Sitzber. Akad. Wien*, **44**. 164, 1862; *Journ. prakt. Chem.*, (1), **86**. 227, 1862; *Bull. Soc. Chim.*, (1), **5**. 197, 1863; H. Copaux, *Compt. Rend.*, **148**. 633, 1909; *Ann. Chim. Phys.*, (8), **17**. 207, 1909; (8), **26**. 32, 1912; *Zeit. anorg. Chem.*, **74**. 351, 1912; S. M. Tanatar and E. Kurowsky, *Journ. Russ. Phys. Chem. Soc.*, **41**. 813, 1909; A. Rosenheim and F. Kohn, *Zeit. anorg. Chem.*, **69**. 247, 1911; J. C. G. de Marignac, *Ann. Chim. Phys.*, (3), **59**. 61, 1863; E. F. Smith, *Chem. News*, **135**. 113, 129, 1927.

§ 26. Phosphotungstic Acids.—Phosphatotungstic Acids and their Salts

Tungsten trioxide was found by F. de Carli[1] to behave like molybdenum trioxide when admixed with sodium metaphosphate. The fusion curve has two minima and a maximum at 850° corresponding with **sodium tungstatometaphosphate,** $NaPO_3.WO_3$, or $Na.O.WO_2.O.PO_2$. The first minimum is at 350° corresponding with 30 per cent. of sodium metaphosphate.

The history of the **tungsten phosphates** commences in 1872 when C. Scheibler[2] observed that a soln. of sodium tungstate containing phosphoric acid is able to precipitate certain organic compounds; and isolated two acids which contained, as he supposed, $P_2O_5 : WO_2$ in the ratios 1 : 22 and 1 : 20 respectively. The barium salt in the first case was derived from the normal sodium tungstate and in the second case from the paratungstate. E. Zettnow reported a number of salts of these acids. O. W. Gibbs suggested that the second acid has the formula $H_{16}P_2W_{21}O_{73}.nH_2O$, and he postulated the existence of six series of these acids in which 24, 22, 20, 18, 16, and 14 mols. of WO_3 are present per mol. of P_2O_5. Acids corresponding with all the members of the series have not been prepared, and other acids containing less tungstic acid have been reported. The general result of the work on these **phosphatotungstic acids** is to show that they are heteropoly-acids closely analogous with the phosphatomolybdic acids. The following phosphatotungstic acids have been reported, although their claims for recognition as chemical individuals have not, in all cases, been established:

Phosphatododecatungstic acid	$P_2O_5.24WO_3.nH_2O$
Phosphatohenatungstic acid	$P_2O_5.22WO_3.nH_2O$
Phosphatohemihenicositungstic acid	$P_2O_5.21WO_3.nH_2O$
Phosphatodecatungstic acid	$P_2O_5.20WO_3.nH_2O$
Phosphatoenneatungstic acid	$P_2O_5.18WO_3.nH_2O$
Phosphatohemiheptadecatungstic acid . . .	$P_2O_5.17WO_3.nH_2O$
Phosphatoctotungstic acid	$P_2O_5.16WO_3.nH_2O$
Phosphatohexatungstic acid	$P_2O_5.12WO_3.nH_2O$
Phosphatohemiheptatungstic acid	$P_2O_5.7WO_3.nH_2O$
Phosphatotritungstic acid	$P_2O_5.6WO_3.nH_2O$

The first number of the series, **phosphatododecatungstic acid,** $P_2O_5.24WO_3.nH_2O$, $H_7[P(W_2O_7)_6].nH_2O$, belongs to a group of heteropoly acids represented by $H_7[P(Mo_2O_7)_6]$, $H_7[As(Mo_2O_7)_6]$, and $H_7[As(W_2O_7)_6]$. This acid is that commonly understood as *phosphotungstic acid.* The following mode of preparation is due to F. Kehrmann :

Phosphatododecatungstic acid is prepared by dissolving 100 grms. of normal sodium tungstate and 15 grms. of crystalline sodium hydrophosphate in a large proportion of boiling water ; and adding hydrochloric acid while the liquid is vigorously stirred so that the crystalline powder which may separate is all dissolved by the boiling water. A conc. soln. of 20 grms. of barium chloride is then added to the liquid. The cold liquid is then heated to boiling, and 10 grms. of barium chloride are added. The precipitated barium salt is washed with cold water, and purified by recrystallization from boiling water. The barium salt in soln. is then treated with the calculated amount of sulphuric acid, and the filtrate evaporated for crystallization.

E. Drechsel recommended the following process :

Phosphatododecatungstic acid is obtained by dissolving 500 grms. of sodium tungstate and 250 grms. of sodium hydrophosphate in 500 c.c. of water, and evaporating the liquid until a skin forms on the surface. 700 to 800 c.c. of hydrochloric acid, of sp. gr. 1·14, are then added to the boiling soln., which is again evaporated, and allowed to cool. The whole is gradually treated with pure ether, being well shaken all the time, until a layer is formed above the acid soln. It is left until the lower layer is clear, then separated and treated with an equal vol. of water ; the ether is then evaporated ; if the soln. becomes bluish, chlorine-water is added. It is evaporated to dryness, dissolved in hot water ; and on cooling, the acid separates in splendid crystals.

The literature has a strangely indefinite answer to the question : What hydrates are formed by phosphatododecatungstic acid ? P. F. M. Sprenger reported the 19½-*hydrate,* from the soln. obtained from silver tungstate mixed with the calculated amount of phosphoric acid, and treated with hydrochloric acid ; O. W. Gibbs, the 20-*hydrate,* by treating a soln. of potassium phosphatoenneatungstate with mercurous nitrate, and afterwards adding hydrochloric acid ; M. Soboleff, the 22½-*hydrate,* by rapidly cooling a supersaturated soln.—*vide infra ;* C. H. Brandhorst and K. Kraut, the 23¼-*hydrate,* by treating a soln. of 100 grms. of crystalline sodium phosphatododecatungstate in 40 c.c. of water with nitric acid of sp. gr. 1·5 ; O. W. Gibbs, the 26½-*hydrate,* by evaporating, in vacuo, the liquid obtained by treating the mercurous salt with hydrochloric acid ; and C. H. Brandhorst and K. Kraut, by adding hydrochloric acid to a soln. of the sodium salt, extracting the acid with alcohol-free ether, and evaporating off the ether ; E. Péchard, the 29½-*hydrate,* from a mixture of eq. proportions of phosphoric and metatungstic acids and evaporating in vacuo ; and P. F. M. Sprenger, the 30½-*hydrate,* by evaporating the soln. obtained by treating the barium salt with sulphuric acid—and a little nitric acid—first on a water-bath and afterwards in vacuo ; and O. W. Gibbs, by evaporating an aq. soln. of the acid in vacuo over sulphuric acid. With the co-ordination formula $H_7[P(W_2O_7)_6].nH_2O$, these hydrates correspond with $n=16$, 16½, 19, 20, 23, 26, and 27.

H. Copaux concluded that there are only the three hydrates of the $H_7[P(W_2O_7)_6]$-acid, *viz.,* (i) the 27½-*hydrate* which separates in octahedra from conc. aq. soln. at about 35° ; (ii) the 22-*hydrate* which separates from a hot, sat. soln. acidified with a little nitric acid, and rapidly cooled ; and (iii) the 19-*hydrate* which crystallizes from a cold soln. strongly acidified with nitric acid. A. Rosenheim and J. Jänicke found that when a conc. aq. soln. is crystallized at ordinary temp., the *octocosihydrate,* $H_7[P(W_2O_7)_6].28H_2O$, *i.e.* $P_2O_5.24WO_3.63H_2O$, is formed, in octahedral crystals. This hydrate is probably the same as the 27½-hydrate of H. Copaux, and it is unstable at ordinary temp. and readily passes into trigonal crystals of the *docosihydrate,* $H_7[P(W_2O_7)_6].22H_2O$, *i.e.* $P_2O_5.24WO_3.51H_2O$. This hydrate, also obtained by H. Copaux, is deposited at ordinary temp. from soln. feebly acidified with nitric acid. The octocosihydrate loses $24H_2O$ in vacuo over sulphuric acid at room temp., and the docosihydrate loses its $22H_2O$ under similar conditions. The transition temp. between these two hydrates is assumed to be somewhere below 0°. If the aq. soln. be strongly acidified with nitric acid, the *enneadecahydrate*, $H_7[P(W_2O_7)_6].19H_2O$, *i.e.* $P_2O_5.24WO_3.45H_2O$, is formed. This is probably the hydrate prepared by H. Copaux, and M. Soboleff.

In agreement with the fact that many of the metal salts have the general formula $R_3'PW_{12}O_{40}nH_2O$, M. Soboleff represented the acid by the formula $H_3PO_4.12WO_3.21H_2O$, to indicate that the acid is tribasic; and P. F. M. Sprenger employed the formula $PO(O.WO_2.O.WO_2.O.WO_2.O.WO_2.OH)_3$. A. Rosenheim, and R. Häberle showed that the eq. conductivity of the guanidinium salt agrees better with the assumption that the acid is heptabasic rather than tribasic. A. Rosenheim and J. Jänicke found that the acid dried in vacuo over sulphuric acid has the composition $P_2O_5.24WO_3.7H_2O$. All this supports the hypothesis that the formula for the acid is $H_7[P(W_2O_7)_6].nH_2O$. A. Miolati and R. Pizzigheli measured the electrical conductivity of soln. of phosphatodecatungstic acid (0·0473 grm. $H_3PO_4.12WO_3.7H_2O$ per c.c.) and of sodium hydroxide (0·0008212 grm. NaOH per c.c.) at 25° when 1 c.c. of the NaOH soln. has 0·1304 mol of NaOH per mol of the acid. The curve has two breaks corresponding with $H_3PO_4.12WO_3.7H_2O : NaOH=1 : 6$ and $1 : 26$. This shows that phosphatododecatungstic acid is at least hexabasic. A. Rosenheim and J. Jänicke's neutralization curve also has a minimum with 6·1 mols. of NaOH per mol. of $H_7[P(W_2O_7)_6].nH_2O$. If the formula $H_7[P(W_2O_7)_6].nH_2O$ be correct, the acid is probably heptabasic. This agrees with the guanidinium salt, $(CN_3H_6)_7[P(W_2O_7)_6].12H_2O$, prepared by A. Rosenheim and J. Jänicke by adding guanidinium carbonate to the free acid; and this is in agreement with the conductivity data. Only acid or hydro-salts of the metals have been prepared. The acid character of the salts is confirmed by conductivity data. The break in the curve with 26 mols. of NaOH corresponds with the formation of the normal tungstate. L. Malaprade found that in the electrometric neutralization of phosphotungstic acid, the general behaviour is the same as in the case of phosphomolybdic acid, but the decomposition of the normal salt begins before an inflexion of the curve occurs.

It is not easy to identify the hydrates reported above with those obtained by H. Copaux, and A. Rosenheim and J. Jänicke. The crystals are in all cases colourless or tinged pale yellow. O. W. Gibbs' and P. F. M. Sprenger's $30\frac{1}{2}$-hydrate was described as forming colourless octahedra which rapidly effloresced in air. These crystals probably represent H. Copaux's, and A. Rosenheim and J. Jänicke's octocosihydrate. E. Péchard's crystals—possibly A. Rosenheim and J. Jänicke's and H. Copaux's docosihydrate—measured by E. Dufet, were said to be cubic octahedral combinations of trigonal crystals with the axial ratio $a : c=1 : 1·2648$, and $\alpha=88° 46'$. M. Soboleff's crystals of presumably the $19\frac{1}{2}$-hydrate were definitely stated to belong to the cubic system. He said:

> The supersaturated soln., when quickly cooled, gives skeleton crystals belonging to the regular system, and then well-formed cubes and octahedra; the last form is the most stable, and is always obtained on cooling saturated soln., or by prolonged crystallization in a desiccator. When these octahedra are separated from the soln., they quickly become covered with six-sided stars, arranged parallel to the edges of the octahedron, and the crystals break up into new crystals which contain less water. The crystals of the second hydrate are obtained by crystallizing a supersaturated soln. in a thermostat at 50°.

The second hydrate furnishes rhombic crystals with the axial ratios $a : b : c = 0·94207 : 1 : 1·96187$, and with the optical character negative. When the soln. is quickly evaporated, long, thin needles are obtained which act on polarized light. If these crystals had effloresced a little before analysis, they probably represented the enneadecahydrate of H. Copaux, and A. Rosenheim and J. Jänicke. The subject is somewhat confused because it is lacking in precise data. M. Soboleff gave 4·68 for the sp. gr. of, presumably, the enneadecahydrate; and for the sp. gr. of sat. aq. soln. at 0°, 1·189; at 22°, 1·6913; at 43°, 1·8264; and at 92°, 2·5813. He also found that soln. of 0·2983, 5·930, and 25·192 grms. of the acid in 100 c.c. of water lower the f.p. of water respectively 0·0146°, 0·1360°, and 0·4710°. The depression with the complex acid was found to be much less than the sum of the effects of the components. At high concentrations, the difference is a constant, 0·023, but at low concentrations the difference is less 0·013. The acid lost 0·11 per cent., or 4·09 mols. of water by efflorescence in air ; and at :

	50°	100°	150°	200°	300°	350°	Red-heat
Percentage loss .	4·40	5·75	6·91	9·29	10·17	10·23	12·42
Mols lost . .	15·3	20·1	24·3	34·1	37·3	37·4	45·00

The acid is freely soluble in water, and, as indicated above, the soln. have a large sp. gr. ; the solubility, *S* grms. of $P_2O_5.24WO_3.45H_2O$, per 100 c.c. of water, is :

	0°	22°	43°	92°
S . .	16·206	49·718	53·64	86·75

while the solubility in ether, *S* grms. of $P_2O_5.24WO_3.45H_2O$ per 100 c.c. of ether, is :

	0°	7·8°	18·2°	24·2°
S . .	81·196	85·327	96·017	101·348

O. W. Gibbs found that the aq. soln. is a colourless oily liquid with a high index of refraction and it has an acidic and bitter taste ; it easily drives carbon dioxide from carbonates. When the aq. soln. has stood for a day, decomposition occurs, and a white, crystalline powder is precipitated. The same powder is always formed in the preparation of the acid. E. Drechsel found that the ethereal soln. can be mixed with alcohol in all proportions, and a soln. with equal vols. of ether and alcohol is not rendered turbid by one vol. of hydrochloric acid, but another vol. of the acid does render the soln. turbid. The ethereal soln. can be mixed with much water without becoming turbid. According to A. Miolati and R. Pizzigheli, with methyl orange as indicator, in the titration of the acid, 6 mols. of NaOH are consumed per mol. of acid $H_7[P(W_2O_7)_6].nH_2O$; and with phenolphthalein as indicator, 26 mols. of NaOH are consumed—*vide supra.* E. Brauer gave $[H^{\cdot}]=0\cdot0041$ for the hydrogen ion concentration of a $0\cdot005N$-soln. of the acid. M. Soboleff found the electrical conductivity of the aq. soln. to be smaller than that of its components ; A. Rosenheim and J. Jänicke found the electrical conductivity, λ mhos, of soln. of $\frac{1}{7}H_7[P(W_2O_7)_6].22H_2O$ in v litres of water at 25° to be :

v .	16	32	64	128	256	512	1024
λ .	160·8	168·9	181·0	198·4	220·3	249·3	274·5

T. G. y Arnal discussed the reactions of phosphotungstic acid with various salts. Phosphatododecatungstic, phosphododecatungstic, or simply phosphotungstic acid forms ammonium, alkali, alkaline earth, silver and mercurous salts of the type $R_2O.P_2O_5.24WO_3.nH_2O$. According to F. Kehrmann and co-workers, if the acid or a salt is mixed with a large excess of a strong base, the first decomposition product is a salt of the formula $7R_2O.P_2O_5.22WO_3.nH_2O$, and a large excess produces tribasic phosphate, and dibasic tungstate, Fig. 51. According to O. W. Gibbs, the phosphatotungstates are only decomposed a little by hydrogen sulphide, and the reduction by zinc is incomplete. Mercurous nitrate gives an almost complete precipitation of the mercurous salt which is yellow, and almost insoluble in water, and sparingly soluble in dil. nitric acid. Owing to the low solubility of the potassium and ammonium salts, phosphotungstic acid could be used for their detection. Many alkaloids give almost insoluble more or less crystalline

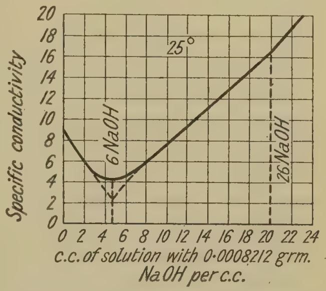


FIG. 51.—Neutralization Curve of Phosphatododecatungstic Acid with Sodium Hydroxide.

precipitates. C. Scheibler said that bulky precipitates are obtained with liquids containing $\frac{1}{200,000}$th of strychnine, or $\frac{1}{100,000}$th of quinine; and he said that the acid can be used as an antidote to poisoning with the organic bases. Egg-albumen also gives a white precipitate, and it is accordingly used as a reagent for precipitating these substances. The behaviour of phosphotungstic acid or the phosphotungstates towards various organic substances was examined by C. Scheibler, E. Winterstein, E. Schulze and E. Winterstein, E. Wechsler, L. Bleibtreu, J. Sebelien, A. von Bäyer and V. Villiger, F. Mylius, H. Moreigne, Z. H. Skraup and co-workers, M. Barber, H. and L. Pellet, P. A. Levene and W. A. Beatty, W. A. Jacobs, L. Guglialmelli, O. Folin and W. Denis, C. Funk and co-workers, J. C. Drummond, A. Heiduschka and L. Wolf, L. Lematte and co-workers, etc. The acid gives white precipitates with substances containing urea, and is used as a clarifying agent in urine analysis—B. Oppler, C. E. May, O. Folin and A. B. Macallum, and C. Funk and A. B. Macallum. The acid is also used for precipitating peptones, and for separating them from acid amido-compounds—A. Stutzer, S. Bondzynsky, A. Vivian, and L. L. van Slyke and E. B. Hart.

O. W. Gibbs prepared **ammonium phosphatododecatungstate,** $3(NH_4)_2O.P_2O_5.24WO_3.29H_2O$, or $(NH_4)_3H_4[P(W_2O_7)_6].12\frac{1}{2}H_2O$, in white or pale yellow crystals, by mixing a soluble ammonium salt with a soln. of mixed sodium tungstate and hydrophosphate, and adding an excess of nitric or hydrochloric acid. F. Kehrmann added a soluble ammonium salt to a dil. soln. of the acid or a salt. F. Kehrmann and E. Böhm found that this salt is also formed when ammonium phosphatohemiheptadecatungstate is treated with dil. hydrochloric acid.

O. W. Gibbs made **sodium hydrophosphatododecatungstate,** $2Na_2O.P_2O_5.24WO_3.27H_2O$, or $Na_2H_5[P(W_2O_7)_6].11H_2O$, by adding an excess of hydrochloric or nitric acid to a soln. of 12 mols. of sodium tungstate and one mol. of sodium hydrophosphate; and C. H. Brandhorst and K. Kraut, used the following process:

750 grms. of hydrochloric acid, of sp. gr. 1·175, diluted with 4 vols. of water, were slowly added, with stirring, to a soln. of a kilogram of sodium tungstate and 100 grms. of sodium hydrophosphate in 4 litres of water, and the soln. evaporated to dryness. $2\frac{1}{2}$ litres of a mixture of equal vols. of alcohol and ether is poured over the mixture, and after 24 hrs., the sodium chloride is filtered off, and the filtrate distilled. The residue is treated with a litre of water and warmed with bromine-water or nitric acid and allowed to stand. The clear soln. is evaporated for crystallization, and recrystallized from water.

The large, colourless or pale yellow crystals are either monoclinic or triclinic, and, according to C. H. Brandhorst and K. Kraut, have a sp. gr. 4·722. The salt is freely soluble in water, and at 20°, the sp. gr. of the soln. with the following proportions of the anhydrous salt, are:

	5	15	25	35	45	55
Sp. gr. .	1·044	1·143	1·262	1·414	1·613	1·872

The salt is more soluble in alcohol than it is in water. The aq. soln., said O. W. Gibbs, gives a white, crystalline precipitate with silver nitrate; and precipitates with barium chloride, and ammonium nitrate after standing some time. With sufficient sodium carbonate the salt is resolved into normal sodium tungstate and phosphate.

F. Kehrmann and co-workers prepared **sodium phosphatododecatungstate,** $3Na_2O.P_2O_5.24WO_3.nH_2O$, as described above in connection with the addition of barium chloride, is recrystallized from boiling water a number of times. This is one of the salts prepared by C. Scheibler—*vide supra.* F. Kehrmann and co-workers showed that if a hot, sat. soln. be cooled, it furnishes colourless, octahedral crystals with cube faces of the *enneadecahydrate*, $Na_3H_4[P(W_2O_7)_6].19H_2O$. The crystals readily effloresce in air, and the salt is very soluble in water. Soln. sat. at 0°, 22°, and 93° were found by M. Soboleff to dissolve respectively 22·04, 59·65, and 98·184 grms. of the crystallized acid per 100 c.c. of water. F. Kehrmann found that the salt is less soluble in hydrochloric acid, and in soln.

of sodium chloride. F. Kehrmann and co-workers found that if the preceding hydrate be allowed to stand in the cold mother-liquor, it slowly dissolves, and the soln. deposits colourless plates which M. Soboleff found to be the tridecahydrate, $Na_3H_4[P(W_2O_7)_6].13H_2O$, and to be triclinic pinacoids with the axial ratios $a:b:c=1\cdot0875:1:2\cdot0814$, and $\alpha=85° 21'$, $\beta=95° 28'$, and $\gamma=87° 41\cdot5'$. The same hydrate is obtained by keeping a conc. soln. at a temp. below 50°. According to C. H. Brandhorst and K. Kraut, if an aq. soln. of the hydrophosphatododecatungstate be shaken with ether, the *enneahydrate*, $Na_3H_4[P(W_2O_7)_6].9H_2O$, is formed as a white powder. E. Hartmann prepared *sodium phosphatododecatungstatomolybdate*, $3Na_2O.P_2O_5.24(MoO_3,WO_3).nH_2O$. According to F. Kehrmann, **potassium phosphatododecatungstate,** $K_3H_4[P(W_2O_7)_6].nH_2O$, is formed when a soluble potassium salt is added to a dil. soln. of the acid or a soluble salt. O. W. Gibbs obtained the *hemiheptahydrate* or the *hemitridecahydrate* by double decomposition with a soluble potassium salt, and the sodium salt, or, as in the analogous case of the sodium salt, by adding hydrochloric or nitric acid to a mixed soln. of potassium phosphate and tungstate. O. W. Gibbs prepared a salt, $4K_2O.P_2O_5.24WO_3.20H_2O$, from a soln. of metaphosphoric acid and potassium pentatungstate. P. F. M. Sprenger, and F. Kehrmann prepared **copper phosphatododecatungstate,** $Cu_3\{H_4[P(W_2O_7)_6]\}_2.54H_2O$, by treating copper carbonate with the calculated quantity of the acid, and evaporating the clear soln. in vacuo. The green, cubic crystals are freely soluble in water. P. F. M. Sprenger, and F. Kehrmann also prepared **silver phosphatododecatungstate,** $Ag_3H_4[P(W_2O_7)_6].26H_2O$, by adding silver nitrate to a dil. soln. of the acid. The white powder is sparingly soluble in water. P. F. M. Sprenger reported **barium hydrophosphatododecatungstate,** $Ba\{H_6[P(W_2O_7)_6]\}_2.54H_2O$, by evaporating a soln. of the calculated quantity of barium carbonate in the acid; and $BaH_5[P(W_2O_7)_6].27H_2O$ in a similar manner; while O. W. Gibbs prepared barium phosphatododecatungstate, $Ba_3\{H_4[P(W_2O_7)_6]\}_2.42H_2O$, which is produced by the action of barium chloride on a soln. of the sodium salt. The *dotessaracontahydrate* forms colourless, octahedral crystals which rapidly effloresce, and are very soluble in hot water; F. Kehrmann and co-workers also prepared this salt. M. Soboleff obtained the *tetratessaracontahydrate*, $Ba_3\{H_4[P(W_2O_7)_6)\}_2.44H_2O$, in octahedral crystals, and P. F. M. Sprenger also prepared the *tetrapentecontahydrate*, $Ba_3\{H_4[P(W_2O_7)_6]\}_2.54H_2O$, in cubic crystals. C. H. Brandhorst and K. Kraut obtained **sodium barium phosphatododecatungstate,** $NaBaH_4[P(W_2O_7)_6].22H_2O$, by treating a cold soln. of sodium hydrophosphatododecatungstate with freshly precipitated barium carbonate, and adding alcohol to the clear soln. The turbid soln. formed by water becomes clear on the addition of hydrochloric acid. F. Kehrmann and M. Freinkel obtained yellow prisms of **silver barium phosphatododecatungstate,** by adding silver nitrate to a soln. of ammonium barium phosphatododecatungstate. O. W. Gibbs added mercurous nitrate to a soln. of 24 mols. of sodium tungstate, and 2 mols. of sodium hydrophosphate, acidified with nitric acid, and obtained a yellow precipitate of **mercurous phosphatododecatungstate,** which is insoluble in water, and slightly soluble in dil. nitric acid. H. Copaux said that the composition is not constant, but varies with the mode of preparation. F. Kehrmann prepared **mercuric phosphatododecatungstate,** $3HgO.P_2O_5.24WO_3.nH_2O$, freely soluble in water, and **lead phosphatododecatungstate,** $3PbO.P_2O_5.24WO_3.nH_2O$.

O. W. Gibbs found that a boiling soln. of sodium phosphatododecatungstate readily dissolves platinic hydroxide forming an orange liquid, which, when filtered and evaporated, furnishes orange crystals of, presumably, **platinic phosphatododecatungstate.** Ammonium chloride precipitates orange yellow crystals from the soln.—presumably ammonium **platinic phosphatododecatungstate.**

P. F. M. Sprenger reported that he had obtained a soln. of **phosphatohenatungstic acid,** $P_2O_5.22WO_3.nH_2O$, by the action of dil. sulphuric acid on the barium salt. The acid itself, however, has not been isolated. Strong mineral acids decompose the salts into the phosphatododecatungstates and the phosphatohemihenacositungstate, and A. Rosenheim and J. Jänicke suggested that the molecule has two nuclei $H_7[P(OH)(W_2O_7)_5]$ linked by a bivalent W_2O_7-bridge, thus:

$$H_7[P(OH)(W_2O_7)_5]\text{–}W_2O_7\text{–}[(W_2O_7)_5(OH)P]H_7\text{–}nH_2O.$$

By treating barium phosphatohemiheptatungstate with sulphuric acid, C. Scheibler obtained an acid which he represented by the formula $H_{11}PW_{11}O_{43}.18H_2O$. O. W. Gibbs reported **ammonium phosphatohenatungstate,** $3(NH_4)_3O.P_2O_5.22WO_3.21H_2O$, to be formed from a mixture of sodium tungstate and hydrophosphate, ammonium nitrate, and an excess of hydrochloric acid. The colourless crystals are freely soluble in cold water, and partially soluble in hot water to form a turbid liquid. The properties of the salt are, in general, like those of the phosphatododecamolybdate. This may be a phosphatododecatungstate. F. Kehrmann prepared the ammonium salt, $7(NH_4)_2O.P_2O_5.22WO_3.nH_2O$, by adding an excess of ammonium carbonate to a boiling conc. soln. of ammonium phosphatododecatungstate so long as effervescence occurs. On cooling, octahedral crystals are obtained, very soluble in water. The salt can be purified by recrystallization from water, acidified with acetic acid. O. W. Gibbs prepared **sodium phosphatohenatungstate,** $2Na_2O.P_2O_5.22WO_3.9H_2O$, by adding an excess of hydrochloric or nitric acid to a soln. of 24 mols. of sodium tungstate, and a mol. of sodium hydrophosphate. The white, crystalline powder is sparingly soluble in water. This may be a phosphatododecatungstate. When the barium salt is treated with sodium sulphate, F. Kehrmann and co-workers found that the filtered soln., on evaporation, furnishes acicular crystals of $7Na_2O.P_2O_5.22WO_3.33H_2O$. O. W. Gibbs added hydrochloric or nitric acid to a soln. of potassium phosphatoenneatungstate, when **potassium phosphatohenatungstate,** $2K_2O.P_2O_5.22WO_3.6H_2O$, was formed as a white precipitate very soluble in water. This may be a phosphatododecatungstate. F. Kehrmann and co-workers prepared $7K_2O.P_2O_5.22WO_3.31H_2O$, by the process used for the ammonium salt. L. Duparc and F. Pearce found the axial ratio of the colourless, tetragonal crystals to be $a:c=1:0{\cdot}6053$. According to F. Kehrmann and co-workers, the salt is readily soluble in hot or cold water, but insoluble in alcohol. Crystalline double salts are obtained when salts of the heavy metals are added to its conc. aq. soln. The general formula is $(7-m)K_2O.mRO.P_2O_5.22WO_3.nH_2O$. The salts are readily broken down into simpler phosphatotungstates—*vide infra.* O. W. Gibbs obtained **barium phosphatohenatungstate,** $4BaO.P_2O_5.22WO_3.41H_2O$, by neutralizing with acetic acid a mixed soln. of 24 mols. of sodium tungstate and 2 mols. of sodium hydrophosphate, and adding barium chloride. The prismatic crystals are soluble in hot water; and the hot aq. soln. deposits needle-like crystals on cooling. P. F. M. Sprenger obtained doubly-refracting needles of the salt $7BaO.P_2O_522WO_3.59{\cdot}5H_2O$, by adding to a soln. of phosphatododecatungstic acid to excess of barium hydroxide, and evaporating the clear filtrate. F. Kehrmann and co-workers prepared the salt $7BaO.P_2O_5.22WO_3.53H_2O$ by adding powdered barium carbonate to a boiling, conc. soln. of barium phosphatododecatungstate so long as effervescence occurs. On cooling, the salt separates in octahedra; and it can be purified by crystallization from water acidified with acetic acid. If barium chloride is added to the potassium salt, octahedral crystals of **potassium barium phosphatohenatungstate,** $2K_2O.5BaO.P_2O_5.22WO_3.48H_2O$, are formed; the action of silver nitrate on a soln. of ammonium barium phosphatohenatungstate furnishes **silver barium phosphatohenatungstate,** $3Ag_2O.4BaO.P_2O_5.22WO_3.34H_2O$. They also prepared **potassium mercuric phosphatohenatungstate** in colourless, soluble needles; and **barium mercuric phosphatohenatungstate,** in sparingly soluble crystals. O. W. Gibbs reported white, crystalline **ammonium stannic phosphatohenatungstate,** $2(NH_4)_2O.2SnO_2.P_2O_5.22WO_3.15H_2O$.

According to F. Kehrmann and M. Freinkel, **phosphatohemihenicositungstic acid,** $P_2O_5.21WO_3.33H_2O$, is produced as follows: Potassium phosphatohenatungstate is dissolved in a little water, and, after adding an excess of dil. hydrochloric acid, the soln. is boiled and filtered from the potassium phosphatododecatungstate. The filtrate slowly deposits the potassium salt of the required acid; this is converted into the ammonium salt by the action of ammonium chloride, and the latter mixed into a mush with aqua regia, and the mixture boiled. The salt decomposes with the evolution of nitrogen, and the required acid separates from the soln. on cooling. The acid is also obtained by treating the barium salt with sulphuric acid; on evaporation, phosphatododecatungstic acid first separates, and the mother-liquor yields a crop of hexagonal crystals of the required acid. It is also obtained by treating the potassium salt with acid, and extraction with ether. The acid forms colourless, four-sided prisms. It is extremely soluble in water, and the aq. soln. can be boiled without decomposition; but not so with a soln. of salts of the acid; they are decomposed. Soln. of the acid can be repeatedly evaporated with conc. hydrochloric or nitric acid without decomposition. Unlike phosphatododecatungstic acid, potassium and ammonium phosphatohemihenicositungstates are not sparingly soluble in water; and the colour, crystal form, and solubilities of the salts of phosphatoenneatungstic acid, are very different from those of the salt of phosphatohemihenicositungstic acid. E. Brauer found that the $H^{\cdot}$-ion conc. of $0{\cdot}005N$-soln. of the acid is $[H^{\cdot}]=0{\cdot}0070$. The structure of the acid has not been determined; but the acid is very probably more than sexibasic, for the salts of the type $3K_2O.P_2O_5.21WO_3.nH_2O$ behave as if they were acid salts. This is supported by the electrical conductivity of the potassium salt which gives normal values on the assumption that it is hexabasic or heptabasic. Soln. with an eq. of salt—*i.e.* $\frac{1}{6}(3K_2O.P_2O_5.21WO_3.31H_2O)$ in v litres at 25° have the conductivities:

v .	32	64	128	256	512	1024
λ .	166·8	184·2	202·2	226·3	254·1	285·2 mhos.

If attempts are made to prepare normal salts, the complex anion is broken down. F. Kehrmann and co-workers prepared **ammonium phosphatohemihenicositungstate,** $3(NH_4)_2O.P_2O_5.21WO_3.nH_2O$, by adding ammonium chloride to a soln. of the potassium salt, and repeating the precipitation from lukewarm soln. in dil. hydrochloric acid a number of times so as to get the salt free from potassium salts. The six-sided prisms are decomposed by boiling water. The salt is sparingly soluble in cold water, but more soluble in hot water; it is insoluble in a sat. soln. of ammonium chloride; and soluble in alcohol. If a boiling, conc. soln. of potassium phosphatohenatungstate be treated with dil. hydrochloric acid added drop by drop, with agitation, until no more precipitate is formed, and the soln. is acid, and potassium chloride added to the filtrate, a crystalline precipitate of **potassium phosphatohemihenacositungstate,** $3K_2O.P_2O_5.21WO_3.nH_2O$, is formed. The colourless, six-sided prisms are decomposed by boiling water; the salt is soluble in cold water.

According to E. Péchard, the evaporation of a soln. of one eq. of phosphoric acid with 5 eq. of metatungstic acid furnishes efflorescent regular octahedra of **phosphatodecatungstic acid,** $P_2O_5.20WO_3.62H_2O$, and if these are dissolved in very little water, and the soln. concentrated, less efflorescent, trigonal crystals of $P_2O_5.20WO_3.50H_2O$ with the axial ratio $a:c=1:1{\cdot}2929$ are formed. O. W. Gibbs also obtained the acid by adding nitric acid in excess to a mixed soln. of sodium phosphate and tungstate; but later, he added that the free acid could not be prepared. There is a doubt about the acid and its salts, because the methods of preparation, and the properties described are similar to those required for the phosphatododecatungstates. C. Scheibler also prepared cubic crystals of an acid which he represented by the formula $H_{11}PW_{10}O_{38}.8H_2O$. O. W. Gibbs obtained **sodium phosphatodecatungstate,** $Na_2O.P_2O_5.20WO_3.19H_2O$, in efflorescent colourless needles, by adding a small excess of hydrochloric acid to a soln. of 12 mols. of sodium tungstate and one mol. of sodium phosphate. E. Péchard also described $Na_2O.P_2O_5.20WO_3.25H_2O$, in prismatic crystals obtained by evaporating on a water-bath a soln. of eq. proportions of the free acid and sodium hydroxide. It is easily soluble in water, and insoluble in alcohol. E. Péchard obtained $2Na_2O.P_2O_5.20WO_3.30H_2O$, from a soln. of an eq. of the free acid and 2 eq. of sodium hydroxide; and by the action of metatungstic acid on sodium hydrophosphate. The rhombohedral crystals do not effloresce in air. The salt is soluble in water, and insoluble in alcohol. If heated to 100°, 20 mols. of water are given off. A sat. soln. of an eq. of the free acid and 2 eq. of sodium hydroxide yields regular octahedral crystals of $3Na_2O.P_2O_5.10WO_3.32H_2O$. The salt is soluble in water, and insoluble in alcohol. E. Péchard prepared **potassium phosphatodecatungstate**, $K_2O.P_2O_5.20WO_3.5H_2O$, as in the case of the corresponding sodium salt. The addition of silver nitrate to a soln. of the potassium salt furnishes **silver phosphatodecatungstate.** E. Péchard obtained **calcium phosphatodecatungstate**, $2CaO.P_2O_5.20WO_3.22H_2O$, in efflorescent octahedra by the action of metatungstic acid on calcium hydrophosphate; **barium phosphatodecatungstate**, $2BaO.P_2O_5.20WO_3.27H_2O$, in colourless octahedra, by the action of metatungstic acid on barium hydrophosphate; and by adding 2 eq. of baryta-water to a soln. of one eq. of the free acid; $2BaO.P_2O_5.20WO_3.36H_2O$, in colourless octahedra, by adding barium chloride to a soln. of sodium paratungstate mixed with phosphoric and hydrochloric acids. O. W. Gibbs reported $6BaO.P_2O_5.20WO_3.48H_2O$, to be formed by adding hydrochloric acid to mixtures of sodium tungstate and sodium hydrophosphate in the proportions between 24 to 2 to 12 : 2. The colourless crystals are readily soluble in hot water. E. Péchard prepared colourless, efflorescent octahedra of **magnesium phosphatodecatungstate**, $2MgO.P_2O_5.20WO_3.19H_2O$, by evaporating in vacuo a soln. of 2 eq. of magnesium carbonate and one eq. of the acid; also **lead phosphatodecatungstate**, $2PbO.P_2O_5.20WO_3.6H_2O$, in white needles.

The so-called **luteophosphotungstic acid**—*luteus*, yellow—or **phosphatoenneatungstic acid**, $P_2O_5.18WO_3.42H_2O$, was prepared by F. Kehrmann as follows:

A soln. of 100 grms. of sodium tungstate in sufficient boiling water was mixed with 50 grms. of syrupy phosphoric acid and 50 c.c. of water, and the water renewed as the soln. is boiled until it acquires a yellow colour. 20 c.c. of conc. nitric acid were added drop by drop to the boiling liquid. The cold liquid was treated with powdered ammonium chloride so long as a yellow precipitate was produced. The powder was isolated by suction, dissolved in a little cold water, and again precipitated by ammonium chloride; the operation was repeated twice more. The pale yellow needles were removed from the large lemon-yellow prisms of the ammonium salt of this acid by levigation, and the salt recrystallized. The product is mixed with 3 parts of conc. hydrochloric acid and one part of conc. nitric acid boiled until the ammonia is all expelled. The yellow soln. is evaporated to remove nitric acid; and the product recrystallized from lukewarm water. The acid is also obtained by decomposing the silver salt with hydrochloric acid. The acid can be extracted from its aq. soln. by ether.

The acid forms lemon-yellow, six-sided, triclinic plates which are stable in air, and melt at 28°. A. Rosenheim and J. Jänicke's analysis corresponds with the empirical formula just indicated. F. Kehrmann's analysis gave $41H_2O$, and he thought that the acid is tribasic. When 25 c.c. of a $\frac{1}{32}N$-soln., on the assumption that an eq. of the acid is one-fifth of the mol $P_2O_5.18H_2O.42H_2O$, is treated with n c.c. of $0{\cdot}1N$-NaOH, and the conductivity measured, the values

C.c. 0·1*N*-NaOH	1	2	4	5	6	8	9
	2·754	2·416	1·739	1·402	1·067	1·066	1·148

show a minimum for 4·4 mols. of base to a mol. of acid, meaning that the acid is at least pentabasic. A. Rosenheim and J. Jänicke found that the lowering of the f.p. of aq. soln. corresponds with a decabasic acid. The electrical conductivity of a soln. of one-third of a mol of $P_2O_5.18WO_3.42H_2O$ in v litres of water at 25° is:

v .	16	32	64	128	256	512	1024
λ .	66·23	68·76	71·14	73·57	76·16	78·01	80·14

The guanidinium salt, $5(CN_3H_6)_2O.P_2O_5.18WO_3.18H_2O$, as also is the silver salt, prepared by R. Häberle, agrees with the assumption that the acid is decabasic, although the corresponding molybdate is dodecabasic, but the complex ion of that acid is not so stable. The constitutional formula of the acid is $H_5[P(OH)(W_2O_7)_4]\text{–}W_2O_7\text{–}[P(OH)(W_2O_7)_4]H_5.36H_2O$, or $H_{10}[(HO)(W_2O_7)_4P\text{–}W_2O_7\text{–}P(W_2O_7)_4(OH)].36H_2O$. H. Wu supposed that the acid exists in two isomeric forms. E. Brauer gave for the $H^{\cdot}$-ion conc. in a $0{\cdot}005N$-soln., 0·0041. The acid is freely soluble in water; it is not changed by strong mineral acids; but the least excess of a strong base breaks down the molecule. When the acid is treated with chlorides or nitrates of the bases, it readily forms salts which are usually fairly soluble. Alkaloids and other nitrogenous organic bases give coloured precipitates with this acid. Alkali carbonates break down the salts into phosphatohemiheptadecatungstates; and with strong acids, phosphatododecatungstates may be formed.

O. W. Gibbs reported **ammonium phosphatoenneatungstate,** $2(NH_4)_2O.P_2O_5.18WO_3.11H_2O$, to remain as a white, crystalline mass, when ammonium paratungstate is boiled with a soln. of metaphosphoric acid. F. Kehrmann and co-workers prepared $3(NH_4)_2O.P_2O_5.18WO_3.14H_2O$, in lemon-yellow, triclinic prisms isomorphous with the potassium salt, as indicated above in connection with the preparation of the acid. A. Rosenheim and J. Jänicke gave $(NH_4)_3H_2[P(OH)(W_2O_7)_4–W_2O_7–(W_2O_7)_4(HO)P]H_2(NH_4)_3.11H_2O$ for the formula. The crystals effloresce in dry air, and in consequence of partial reduction become greenish. The ammonium salt is more soluble than the potassium salt. F. Kehrmann reported **sodium phosphatoenneatungstate,** $3Na_2O.P_2O_5.18WO_3.nH_2O$, to be formed in soluble, lemon-yellow, six-sided plates, by evaporating a mixed soln. of sodium tungstate with an excess of phosphoric acid; or by adding sodium sulphate to a soln. of the barium salt. F. Kehrmann prepared **potassium phosphatoenneatungstate,** $3K_2O.P_2O_5.18WO_3.14H_2O$, by adding potassium chloride to a soln. of the acid. A. Rosenheim and J. Jänicke represented the formula $K_3H_2[P(OH)(W_2O_7)_4–W_2O_7–(W_2O_7)_4(OH)P]K_3H_2.11H_2O$. He first represented the formula by $3K_2O.P_2O_5.16WO_3.16H_2O$. The lemon-yellow, triclinic crystals were found by C. Stuhlmann to have the axial ratios $a : b : c = 0·6278 : 1 : 0·9508$, and $\alpha = 80° 26'$, $\beta = 118° 34'$, and $\gamma = 81° 15'$. The salt is freely soluble in water. Like the ammonium salt it is decomposed when treated with potassium carbonate, forming the phosphatohemiheptadecatungstate. O. W. Gibbs reported $K_2O.P_2O_5.18WO_3.19H_2O$ to be formed as a sparingly-soluble, white, crystalline mass on adding an excess of hydrochloric acid to a soln. of the normal salt; and he obtained prismatic crystals of $6K_2O.P_2O_5.18WO_3.23H_2O$, by adding alcohol to a boiling soln. of 20 mols. of sodium tungstate and 2 mols. of sodium hydrophosphate acidified with acetic acid, and then adding potassium chloride to an eq. soln. of the product. If the salt separates from conc. soln. it has $30H_2O$. F. Kehrmann obtained emerald green plates of **copper phosphatoenneatungstate,** $3CuO.P_2O_5.18WO_3.nH_2O$, easily soluble in water. If a soln. of the potassium salt is treated with silver nitrate, **silver phosphatoenneatungstate,** $3Ag_2O.P_2O_5.18WO_3.14H_2O$, is precipitated. A. Rosenheim and J. Jänicke represented it by $Ag_3H_2[P(OH)(W_2O_7)_4–W_2O_7–(W_2O_7)_4(OH)P]H_2Ag_3.13H_2O$; F. Kehrmann at first regarded it as $3Ag_2O.P_2O_5.16WO_3.40H_2O$. If a 30 per cent. soln. of the acid be treated with 5 to 6 molar proportions of sodium hydroxide, a soluble silver salt, a yellow flaky precipitate of $5Ag_2O.P_2O_5.18WO_3.34H_2O$, or $Ag_5[P(OH)(W_2O_7)_4–W_2O_7–(W_2O_7)_4(OH)P]Ag_5.34H_2O$, is formed. It is almost insoluble in water. F. Kehrmann at first regarded it as $5Ag_2O.P_2O_5.16WO_3.nH_2O$. The corresponding guanidinium salts were obtained in an analogous manner. F. Kehrmann found that **barium phosphatoenneatungstate,** $3BaO.P_2O_5.18WO_3.nH_2O$, separates out when barium chloride is added to a conc. soln. of the acid. The pale yellow plates are sparingly soluble in water. F. Kehrmann also prepared **mercuric phosphatoenneatungstate,** $3HgO.P_2O_5.18WO_3.nH_2O$, freely soluble in water; **lead phosphatoenneatungstate,** $3PbO.P_2O_5.18WO_3.nH_2O$, in six-sided plates, soluble in water.

F. Kehrmann and E. Böhm prepared salts of **phosphatohemiheptadecatungstic acid,** $P_2O_5.17WO_3.nH_2O$, by neutralizing a 30 per cent. soln. of phosphatoenneatungstic acid with aq. ammonia or potash-lye, or ammonium or potassium hydrocarbonates, using litmus as an indicator. The yellow colour of the soln. slowly disappears, and, in the case of ammonia, white, cubic, or tabular crystals of **ammonium phosphatohemiheptadecatungstate,** $5(NH_4)_2O.P_2O_5.17WO_3.16H_2O$, separate out. The salt is sparingly soluble in cold water, and when the aq. soln. is boiled the salt is decomposed with the escape of ammonia. The salt is converted by dil. hydrochloric acid into phosphatoenneatungstate and free phosphoric acid. F. Kehrmann seems to have at first regarded these salts as phosphato-octotungstates.

By using a similar process, or by the action of potassium hydrocarbonate on potassium phosphatoenneatungstate, F. Kehrmann, and F. Kehrmann and E. Böhn prepared **potassium phosphatohemiheptadecatungstate,** $5K_2O.P_2O_5.17WO_3.21$ or $22H_2O$, in white plates, sparingly soluble in cold water; and by treating the potassium salt with a soln. of silver nitrate in excess, **silver phosphatohemiheptatungstate,** $5Ag_2O.P_2O_5.17WO_3.20H_2O$, is formed in yellow plates. The salts were also studied by A. Rosenheim and J. Jänicke, but neither the free acid nor salts of a lower basicity are known.

E. Péchard reported **phosphatoctotungstic acid,** $P_2O_5.16WO_3.69H_2O$, to be formed in colourless, cubic octahedra by concentrating in vacuo a soln. of metatungstic and phosphoric acids in theoretical proportions. O. W. Gibbs reported ammonium phosphatoctotungstate, $6(NH_4)_2O.P_2O_5.16WO_3.10H_2O$, to be formed by adding ammonium chloride to a boiling soln. of sodium paratungstate in phosphoric acid. The prismatic crystals are easily soluble in hot water, and the hot soln. deposits crystals of the salt on cooling. O. W. Gibbs also prepared colourless needles of **potassium phosphatoctotungstate,** $4K_2O.P_2O_5.16WO_3.21H_2O$, in colourless needles, soluble in hot water; he reported the complex salt **sodium potassium phosphatoctotungstate,** $2Na_2O.3K_2O.P_2O_5.16WO_3.20H_2O$; and he also prepared **calcium phosphatoctotungstate,** $CaO.P_2O_5.16WO_3.8H_2O$, in colourless, soluble plates. E. Péchard obtained **barium phosphatoctotungstate,** $2BaO.P_2O_5.16WO_3.10H_2O$, by evaporating a soln. of 2 eq. of barium carbonate in the free acid. The regular octahedra are freely soluble in water, and insoluble in alcohol. F. Kehrmann reported insoluble **mercurous phosphatoctotungstate,** $3Hg_2O.P_2O_5.16WO_3.nH_2O$; and **lead phosphatoctotungstate,** $5PbO.P_2O_5.16WO_3.nH_2O$, as a yellow insoluble powder, and $3PbO.P_2O_5.16WO_3.nH_2O$ in yellow prisms or needles; soluble in water; and with an excess of water forming a basic salt. F. Kehrmann also reported $P_2O_5.16WO_3.41H_2O$, as well as the **phosphatoctotungstates** of ammonium, potassium, and silver salts, but improved analytical methods showed that the products were phosphatohemiheptadecatungstates, or phosphatoenneatungstates.

E. Péchard found that **phosphatohexatungstic acid,** $P_2O_5.12WO_3.42H_2O$, is the most easily prepared of all the phosphotungstic acids. It is obtained by concentrating in vacuo a soln. of metatungstic and phosphoric acids in theoretical proportions. The triclinic, pinacoidal crystals were found by E. Dufet to have the axial ratios $a:b:c=0{\cdot}9916:1:1{\cdot}5931$, and $\alpha=90°\ 6'$, $\beta=97°\ 53\frac{1}{2}'$, and $\gamma=84°\ 25\frac{1}{2}'$. The (110)-cleavage is marked. The crystals do not effloresce in air; and are soluble in water and alcohol. Warm acids decompose the acid liberating tungstic acid; and with bases, it forms salts. An excess of alkali decomposes the salts forming a tungstate and a phosphate. The salts are prepared by treating the acid with a carbonate of the base, or by the action of metatungstic acid on a phosphate. E. Péchard said that **ammonium phosphatohexatungstate,** $2(NH_4)_2O.P_2O_5.12WO_3.5H_2O$, is insoluble in cold water, an excess of aq. ammonia converts it into ammonium paratungstate. A soln. of the acid treated with 2 eq. of lithium carbonate furnishes trigonal crystals of **lithium phosphatohexatungstate,** $2Li_2O.P_2O_5.12WO_3.21H_2O$. The triclinic pinacoids of **sodium phosphatohexatungstate,** $2Na_2O.P_2O_5.12WO_3.18H_2O$, were obtained in a similar manner. E. Dufet found that the crystals have imperfect (110)-, and (001)-cleavages. The crystals effloresce slowly in air. The salt is soluble in water, and is precipitated from its aq. soln. by alcohol. Conc. hydrochloric acid gives a white crystalline precipitate. If hydrochloric acid be left in contact with the salt, or if the salt be treated with warm acid, it is decomposed. White, insoluble potassium phosphatohexatungstate, $K_2O.P_2O_5.12WO_3.9H_2O$, was prepared in a similar manner. E. Péchard also prepared green, trigonal crystals of **copper phosphatohexatungstate,** $2CuO.P_2O_5.12WO_3.11H_2O$, which E. Dufet found had the axial ratio $a:c=1:2{\cdot}6534$, and $\alpha=56°\ 30'$. E. Péchard obtained **silver phosphatohexatungstate,** $Ag_2O.P_2O_5.12WO_3.8H_2O$, as a white insoluble precipitate stable in light; trigonal crystals of **calcium phosphatohexatungstate,** $2CaO.P_2O_5.12WO_3.19H_2O$, which rapidly effloresce in air, and are insoluble in alcohol. E. Dufet gave for the axial ratio $a:c=1:2{\cdot}6759$, and $\alpha=56^\circ\ 8'$. E. Péchard prepared trigonal crystals of **barium phosphatohexatungstate,** $2BaO.P_2O_5.12WO_3.15H_2O$, which, according to E. Dufet, have the axial ratio $a:c=1:2{\cdot}6839$, and $\alpha=56^\circ\ 1'$. The salt effloresces rapidly in air; it is stable in water; and is precipitated by alcohol from its aq. soln. The trigonal crystals of **magnesium phosphatohexatungstate,** $2MgO.P_2O_5.12WO_3.10H_2O$, prepared by E. Péchard were found by E. Dufet to have the axial ratio $a:c=1:2{\cdot}6523$, and $\alpha=56^\circ\ 23'$. E. Péchard also prepared trigonal crystals of **zinc phosphatohexatungstate,** $2ZnO.P_2O_5.12WO_3.7H_2O$; sparingly soluble **cadmium phosphatohexatungstate,** $2CdO.P_2O_5.12WO_3.13H_2O$; and yellow, **mercurous phosphatohexatungstate,** $Hg_2O.P_2O_5.12WO_3.nH_2O$, insoluble in nitric acid. E. Péchard obtained a white precipitate of **thallous phosphatohexatungstate** by the action of metaphosphoric and tungstic acids on thallous carbonate. White, insoluble needles of **lead phosphatohexatungstate,** $2PbO.P_2O_5.12WO_3.6H_2O$, were prepared.

According to F. Kehrmann and R. Mellet, when a very conc. soln. of a mixture of sodium tungstate and phosphate is faintly acidified with acetic acid, and allowed to stand a few days, a mass of crystals is formed. When washed with cold water, there remains a sparingly-soluble *sodium phosphatotungstate,* $14Na_2O.5P_2O_5.19WO_3.nH_2O$, or $29Na_2O.10P_2O_5.39WO_3.nH_2O$. The soluble portion contains a phosphatotritungstate—*vide infra.* O. W. Gibbs reported a complex *sodium potassium phosphatotungstate,* $7Na_2O.11K_2O.6P_2O_5.22WO_3.42H_2O$.

O. W. Gibbs reported **sodium phosphatohemiheptatungstate,** $5Na_2O.2P_2O_5.14WO_3.42H_2O$, to be formed by boiling sodium paratungstate with less than half its weight of syrupy phosphoric acid. Colourless, prismatic crystals are deposited in a few days. The salt may be a mixture. F. Kehrmann reported $3Na_2O.P_2O_5.7WO_3.nH_2O$ to be formed by the action of a cold sat. soln. of sodium tungstate on aq. phosphoric acid, and allowing the acid liquid to stand for a month at ordinary temp. C. Scheibler reported crystals of sodium phosphotungstate, $Na_5H_{11}P_2W_6O_{31}.13H_2O$, to be formed by dissolving sodium paratungstate in water, adding half its weight of phosphoric acid, and allowing the mixture to stand for some time. F. Kehrmann and R. Mellet showed that the salt is really a sodium phosphatohemiheptatungstate, $3Na_2O.P_2O_5.7WO_3.nH_2O$. F. Kehrmann treated a soln. of this salt with ammonium chloride for a number of times in the cold, and obtained **ammonium phosphatohemiheptatungstate,** $3(NH_4)_2O.P_2O_5.7WO_3.nH_2O$, in cubic crystals which are deposited when the aq. soln. is treated with alcohol. The salt is sparingly soluble in cold water without decomposition, but with boiling water, ammonia is evolved. The aq. soln. with a calcium salt gives after standing some time a sparingly-soluble, crystalline **ammonium calcium phosphatohemiheptatungstate;** with barium chloride, sparingly soluble **barium phosphatohemiheptatungstate** is precipitated. C. Scheibler prepared barium phosphatohemiheptatungstate by the action of barium chloride on the sodium salt which he prepared. F. Kehrmann found that a soln. of ammonium or sodium phosphatohemiheptatungstate with silver nitrate, furnishes white insoluble **silver phosphatohemiheptatungstate.** It dissolves in a soln. of the ammonium salt forming **ammonium silver phosphatohemiheptatungstate.**

F. Kehrmann and R. Mellet did not succeed in preparing **phosphatotritungstic acid,** but, as indicated above, they found that the aq. filtrate obtained from sodium phosphatotetratungstate contains a salt which when crystallized out consists of **sodium phosphatotritungstate,** $3Na_2O.P_2O_5.6WO_3.16H_2O$. It is best obtained by the slow crystallization of an aq. soln. of 3 mols. of sodium tungstate, and a mol. of sodium hydrophosphate neutralized with acetic acid. The salt was purified by recrystallization from water. It forms aggregates of white, striated prisms, and contains 3 mols. of water of constitution. The potassium salt could not be prepared directly from its constituents; but when a soln. of the sodium salt is treated with potassium chloride, prismatic needles of **potassium phosphatotritungstate,** $3K_2O.P_2O_5.6WO_3.14H_2O$, are formed; and if ammonium chloride is used, stout prisms of **ammonium phosphatotritungstate,** $3(NH_4)_2O.P_2O_5.6WO_3.9H_2O$, are formed.

O. W. Gibbs prepared a series of **pyrophosphatotungstates** by boiling tungstic acid with an alkali pyrophosphate. The phosphoric acid can be separated from the salts only by boiling them repeatedly with hydrochloric acid. White, granular **potassium pyrophosphatotungstate,** $18K_2O.9P_2O_5.22WO_3.49H_2O$, was so obtained; and **ammonium sodium pyrophosphatotungstate,** $14(NH_4)_2O.6Na_2O.9P_2O_5.22WO_3.31H_2O$, as a white, crystalline precipitate easily soluble in hot water. The potassium salt when treated with copper sulphate furnishes **copper pyrophosphatotungstate,** or a double salt; while mercurous nitrate with the potassium or sodium ammonium salt gives a yellow or white crystalline precipitate of **mercurous pyrophosphatotungstate.** A mixed soln. of sodium paratungstate and manganese pyrophosphate on evaporation yields orange-brown crystals of **sodium manganese pyrophosphatotungstate,** $6Na_2O.3MnO.P_2O_5.14WO_3.36H_2O$; and when this salt is treated with ammonium chloride it furnishes orange prisms of **ammonium sodium manganese pyrophosphatotungstate,** $5(NH_4)_2O.2Na_2O.6MnO.2P_2O_5.14WO_3$, which are soluble in cold and hot water.

REFERENCES.

[1] F. de Carli, *Atti Congres. Chim. Pure Appl.*, 1151, 1926.

[2] C. Scheibler, *Zeit. Naturwiss. Halle*, **40**. 298, 1872; *Bull. Soc. Chim.*, (2), **19**. 23, 1873; *Ber.*, **5**. 801, 1872; O. W. Gibbs, *ib.*, **10**. 1384, 1877; **18**. 1089, 1885; *Bull. Soc. Chim.*, (2), **30**. 31, 1878; (3), **41**. 618, 1884; (3), **14**. 1176, 1895; *Amer. Chem. Journ.*, **2**. 217, 1880; **5**. 361, 1884; **7**. 313, 1886; **17**. 77, 67, 1895; *Proc. Amer. Acad.*, **16**. 109, 1880; **21**. 110, 1885; **30**. 255, 1894; E. Zettnow, *Pogg. Ann.*, **130**. 259, 1867; F. Kehrmann and M. Freinkel, *Ber.*, **24**. 2326, 1891; **25**. 1966, 1892; *Zeit. anorg. Chem.*, **1**. 423, 1892; F. Kehrmann and E. Böhm, *ib.*, **6**. 386, 1894; F. Kehrmann and R. Mellet, *Arch. Sciences Genève*, (4), **41**. 317, 1916; *Helvetica Chim. Acta*, **5**. 942, 1922; **6**. 443, 656, 1923; F. Kehrmann, *Liebig's Ann.*, **245**. 43, 1888; *Zeit. anorg. Chem.*, **1**. 437, 1892; **4**. 138, 1893; **6**. 386, 1894; **7**. 406, 1894; **22**. 290, 1900; *Ber.*, **20**. 1805, 1887; *Bull. Soc. Chim.*, (2), **48**. 502, 1887; (3), **2**. 19, 1889; P. F. M. Sprenger, *ib.*, (2), **36**. 221, 1881; *Ueber Phosphorwolframsäure*, Halle a. S., 1890; *Journ. prakt. Chem.*, (2), **22**. 418, 1880; A. Miolati and R. Pizzigheli, *ib.*, (2), **77**. 417, 1908; E. Péchard, *Compt. Rend.*, **108**. 1167, 1889; **109**. 301, 1889; **110**. 754, 1890; *Ann. Chim. Phys.*, (6), **22**. 226, 1891; *Bull. Soc. Chim.*, (3), **3**. 802, 1890; C. H. Brandhorst and K. Kraut, *ib.*, (2), **36**, 221, 1890; *Liebig's Ann.*, **249**. 373, 1888; M. Soboleff, *Zeit. anorg. Chem.*, **12**. 16, 1896; G. Jander, D. Mojert, and T. Aden, *ib.*, **180**. 129, 1929; A. Rosenheim and J. Jänicke, *ib.*, **77**. 239, 1912; **101**. 254, 1917; A. Rosenheim and E. Brauer, *ib.*, **93**. 284, 1915; E. Brauer, *Ueber die Beständigkeit der Anionen der Heteropolysäuren*, Berlin, 1918; A. Rosenheim, *Zeit. Elektrochem.*, **17**. 696, 1911; R. Häberle, *Zur Kenntnis der Heteropolywolframate*, Berlin, 1911; T. G. y Arnal, *Anal. Soc. Fis. Quim.*, **26**. 435, 1928; L. Malaprade, *Ann. Chim. Phys.*, (10), **9**. 104, 159, 1929; C. Stuhlmann, *Zeit. Kryst.*, **21**. 174, 1893; E. Drechsel, *Ber.*, **20**. 1452, 1887; M. Fremery, *ib.*, **17**. 296, 1884; *Bull. Soc. Chim.*, (2), **42**. 457, 1884; A. von Baeyer and V. Villiger, *Ber.*, **34**. 2679, 1901; F. Mylius, *ib.*, **36**. 775, 1903; H. Copaux, *Zeit. anorg. Chem.*, **74**. 359, 1912; *Ann. Chim. Phys.*, (8), **17**. 251, 1909; (8), **26**. 22, 1912; E. Defacqz, *ib.*, (7), **22**. 238, 1901; *Compt. Rend.*, **132**. 138, 1901; J. Lefort, *ib.*, **92**. 1461, 1881; *Ann. Chim. Phys.*, (5), **25**. 200, 1882; E. Winterstein, *Chem. Ztg.*, **22**. 539, 1898; E. Schulze and E. Winterstein, *Zeit. physiol. chem.*, **33**. 574, 1901; L. Guglialmelli, *Anal. Soc. Quim. Argentina*, **6**. 57, 1918; E. Wechsler, *Zeit. physiol. Chem.*, **73**. 138, 1911; B. Oppler, *ib.*, **75**. 71, 1911; J. Sebelien, *ib.*, **13**. 135, 1888; P. A. Levene and W. A. Beatty, *ib.*, **47**. 149, 1906; W. A. Jacobs. *Journ. Biol. Chem.*, **12**. 429, 1912; C. E. May, *ib.*, **11**. 81, 1912; H. Wu, *ib.*, **43**. 189, 1920; O. Folin and W. Denis, *ib.*, **12**. 239, 245, 1912; O. Folin and A. B. Macallum, *ib.*, **11**. 265, 1912; **13**. 363, 1912; C. Funk and A. B. Macallum, *Biochem. Journ.*, **7**. 356, 1913; C. Funk, *Bull. Biochem.*, **5**. 1, 1916; J. C. Drummond, *Biochem. Journ.*, **12**. 5, 1918; A. Heiduschka and L. Wolf, *Schweiz. Apoth. Ztg.*, **58**. 213, 229, 1920; E. Dufet, *Bull. Soc. Min.*, **13**. 202, 1890; L. Duparc and F. Pearce, *ib.*, **20**. 11, 1897; O. R. Sweeney, *Journ. Amer. Chem. Soc.*, **38**. 2377, 1916; E. Hartmann, *German Pat., D.R.P.* 445151, 1924; L. Bleibtreu, *Pflüger's Arch.*, **44**. 512, 1889; H. and L. Pellet, *Bull. Assoc. Chim. Suer*, **24**. 613, 1906; H. Moreigne, *Ann. Chim. Anal. Appl.*, **10**. 15, 1905; M. Barber, *Monatsh.*, **27**. 379, 1906; Z. H. Skraup, *ib.*, **26**. 1343, 1905; Z. H. Skraup and R. Zwerger, *ib.*, **26**. 1403, 1906; Z. H. Skraup and F. Heckel, *ib.*, **26**. 1351, 1906; A. Stutzer, *Zeit. anal. Chem.*, **35**. 493, 1896; S. Bondzynsky, *Landw. Jahrb. Schweiz*, **8**. 189, 1894; A. Vivian, *Ann. Rep. Wisconsin Exp. Station*, **16**. 171, 1899; L. L. van Slyke and E. B. Hart, *Amer. Chem. Journ.*, **29**. 159, 1903; L. Lematte, G. Boinot, and E. Kahane, *Compt. Rend.*, **191**. 1130, 1930.

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